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THE UNIVERSITY OF ALBERTA

THE DETERMINATION OF ALUMINUM IN AGRICULTURAL MATERIALS

by

NORINE FAY MOTKOSKY

(C)

A Thesis

Submitted To The Faculty Of Graduate Studies And Research

In Partial Fulfilment Of The Requirements For The Degree Of

Master of Science

The Department of Chemistry

Edmonton, Alberta

Fall, 1991

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THE UNIVERSITY OF ALBERTA

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To

Mom and Dad

Thanks for the opportunity to complete this degree and

for your unconditional love and support.

ABSTRACT

Ten agricultural materials, obtained from Agriculture Canada and the U.S. National Institute of Science and Technology, were analyzed for their aluminum content. Because reliable results for trace aluminum are difficult to obtain, three analytical techniques were compared. Graphite furnace atomic absorption spectroscopy (GFAAS) gave reproducible results that showed all of the materials to have a homogeneous distribution of aluminum. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was not sufficiently sensitive under the conditions used. This was due partly to the low aluminum concentrations in the materials and partly to the limited sample sizes that could be dissolved by microwave digestion.

Neutron activation analysis (NAA) gave reproducible results which were high compared to the GFAAS results due to phosphorus and silicon interference. A correction for phosphorus was determined by derivative activation analysis of a solvent-extracted phosphovanadomolybdate complex. Results for the phosphorus analyses were reproducible and standard reference materials determined by this method gave satisfactory results. Correction of the NAA aluminum results for phosphorus interference gave values that agreed with the aluminum values by GFAAS provided that the amount of silicon present was too low to interfere.

Correction of the aluminum values for silicon was difficult. Silicon analyses were first attempted by ICP-AES, but the refractory nature of silicon made it difficult to get reliable results. A GFAAS method for silicon was also attempted but yielded highly scattered and irreproducible values. The final method studied for the determination of silicon was inductively coupled plasma mass spectrometry (ICP-MS). This method gave values for silicon in standard reference materials that were much improved over the

GFAAS method but were still outside the acceptable range owing to interference by N_2^+ on the silicon peak at 28 amu.

Overall, GFAAS appears to be the only method of the three investigated that provides consistent and reliable results for aluminum at levels of a few micrograms per gram in biological materials.

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LIST OF ABBREVIATIONS

DAA	Derivative Activation Analysis
ENAA	Epithermal Neutron Activation Analysis
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
HCL	Hollow Cathode Lamp
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrocopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ISE	Ion Selective Electrode
PIXE	Proton Induced X-ray Emission
CRM	Certified Reference Material
RM	Reference Material
SRM	Standard Reference Material
NIES	National Institute for Environmental Studies
NIST	National Institute for Science and Technology
NRC	National Research Council
EDTA	Ethylenediaminetetraacetic acid
TMAH	Tetramethyl ammonium hydroxide

CHAPTER 1

INTRODUCTION

1.1 THE DETERMINATION OF ALUMINUM IN BIOLOGICAL MATERIALS

1.1.1 Background

Aluminum measurements in biological materials are essential to providing an understanding of the effects of this metal in health and disease. Aluminum is the third most abundant element in the earth's crust. The aluminum uptake of any individual depends on eating habits. It is used as a filler in pickles and cheese, and in antacids for treatment of stomach problems.

Factors that regulate aluminum absorption from the gastrointestinal tract are poorly understood. One major reason for this is the lack of an available isotope to measure aluminum absorption directly (1). Aluminum is excreted primarily by the kidneys. In the last decade it has been found that there is a connection between high aluminum levels in tissue and certain diseases. Patients with renal disease often lack renal function and are unable to excrete absorbed aluminum (1). Treatment of individuals with kidney failure by hemodialysis often produces aluminum toxicity, likely due to aluminum accumulation from the water used in dialysis and from aluminum-containing gels that are used to control serum phosphate levels (2). The aluminum toxicity in these patients usually takes the form of encephalopathy or osteomalacic bone disease.

Encephalopathy is a disorder that affects the brain. Loss of speech, directional disorientation, seizures, hallucinations and dementia (personality changes, confusion, memory loss, etc.) are symptoms of this disease (1). Osteomalacia, the accumulation of aluminum in the bone through displacement of calcium, leads to weakness and broken bones. Aluminum may also accumulate in the parathyroid glands and suppress secretion of parathyroid hormones that control blood calcium levels (1). This will also lead to loss of calcium in the bones. High aluminum levels also affect the blood, producing red blood

cells that are smaller than normal (1). Brain levels of 0.5 μg Al/g are considered normal. Values of 1.5 μg Al/g and above are considered toxic (3).

Aluminum ion concentrations that exceed normal by three-to-five fold are associated with major deficits in the performance of learning and memory tasks, changes in electrical property of brain cells and accumulation of an excessive number of neurofilaments, a histopathological change called neurofibrilary degeneration (NFD) (4). This disorder is often called senile dementia or Alzheimer's disease. Much has been written over the last several years regarding the connection between aluminum and Alzheimer's disease. Two research groups have failed to find a causative connection between aluminum and Alzheimer's disease but it was later found that this was due to a sampling problem (4). Good analytical procedures for the determination of aluminum in biological materials are needed to clarify our understanding of many of these disorders.

1.1.2 Problems with the determination of aluminum

Aluminum is a difficult element to determine at low concentrations in biological materials for a number of reasons. The first and most important reason is that aluminum is ubiquitous. Difficulty arises in collecting, storing, processing and analyzing samples without outside contamination. For example, the range of aluminum concentrations for NIST SRM 1577a Bovine Liver reported in the literature was 1.8 to 65 ppm (5). With such scattered data it is evident that sensitive and reliable methods for trace aluminum determination are not yet available.

1.1.3 Methods for determining aluminum

Aluminum can be determined by many methods. These include gravimetry, titrimetry, spectrophotometry, extraction and various instrumental methods such as X-ray fluorescence, atomic absorption and instrumental neutron activation analysis.

Gravimetry. Aluminum in solution at concentrations above trace levels can be determined gravimetrically as the hydroxyquinolate from either acetate, ammoniacal or water-acetone solutions (6), but precipitation as hydrated aluminum oxide is the most common method of separation.

Precipitation can be done by addition of ammonia, weak organic bases or compounds which release ammonia when heated (6). Examples of reagents used for precipitation of $Al_2O_3\ xH_2O$ include pyridine, α-picoline and urea. Precipitation of aluminum with benzoic acid is one of the most accurate methods. Aluminum can also be precipitated as cryolite, Na_3AlF_6, a sparingly soluble aluminum complex formed if NaF is present. This method is a standard one for the determination of aluminum in alloy steels, and in other ferrous alloys and metals (6).

Titrimetry. Complexometric titrations are the only type commonly used for the determination of aluminum. They are more accurate and less time consuming than gravimetric methods, and are also useful for moderate to large concentrations. Complexometric titrations can be direct or indirect. Direct methods include titration by EDTA in the presence of 1-(2-pyridylazo)-2-napthol as indicator with small amounts of copper-EDTA complex (6). The end point is a sharp change from red to yellow. Aluminum in steels, ferroalloys, etc. has been determined by this very accurate complexometric method.

One example of an indirect method is back titration of excess EDTA with zinc using xylenol orange as indicator. The Al-EDTA complex is formed with excess EDTA. Xylenol orange is added and the excess EDTA is titrated with a standard zinc solution. The color change from yellow to red-violet indicates the formation of the Al-xylenol orange complex and the end point (6). Excess EDTA can also be titrated with standard zinc using dithizone as indicator in a water-ethanol solution (6). This end point is a sharp change from greenish-violet to purple-red. The last two methods are reported to give the sharpest color changes and to be accurate. A third back titration uses Arsenazo III as indicator. An

excess of EDTA is added, then a small amount of La-EDTA, and the excess EDTA titrated with $ZnCl_2$ to a green end point (7).

Aluminum can also be determined by titration with fluoride ions. The formation of sodium hexafluoroaluminate is responsible for the 1:6 stoichiometry (8). Potentiometry with a fluoride ion selective electrode (ISE) has been used for end point detection of this reaction at pH 5 and ionic strength 1.0 (9). A copper ISE has also been used. Excess EDTA is added to the aluminum sample, which is then titrated with a dilute copper solution (10^{-4} M) using the Cu ISE as indicator electrode (10).

In a different approach aluminum was also determined in a potentiometric titration with tetraphenylborate (11). The potential was monitored with a coated graphite sensor and a double junction electrode.

Spectrophotometry. Photometric methods are probably the most numerous of all techniques for determining aluminum. Aluminum complexes with a variety of reagents have been determined at various wavelengths. Complexing ligands reported for this purpose include aluminon (6,12), eriochrome cyanine R (6,13), chrome azurol S (6,14,15), xylenol orange (6,16), pyrocatechol violet (6,12), catechol violet (17) and hydroxyquinoline (6,18). The colored complexes are determined spectrophotometrically; each system is buffered to control pH. Cetylpyridinium standards with (19) and without (20) bromophenyl blue, alizarine complexone (21), beryllon II (22), arsenazo (6,23) and khromazo BRZ (24) (the latter contains OH, SO_3H, azo, napthalene, C_6H_4, and iminodiacetate groups) have also been used. In some cases the colored complex is extracted into an organic phase (10,17,19,21,22) prior to determination.

Morin forms a 1:1 complex with aluminum that gives a green fluorescence (6,25). This method has many disadvantages however and is rarely used. Aluminum hydroxyquinolate produces a green-yellow fluorescence in chloroform and is the basis of the most important fluorescent method for the determination of aluminum (6).

Electrochemistry. Polarographic methods for aluminum are limited to indirect procedures because interferences from oxide formation and solution conditions generally affect the aluminum wave strongly. The solochrome violet complex of aluminum gives a clean polarographic wave (6,26). The aluminum-beryllon II 1:1 complex also shows a nice polarographic wave at -0.46 V(vs SCE) (27). Aluminum can also be determined polarographically using a gold working electrode and a platinum plate counter electrode in the presence of NaEDTA, CuEDTA, ascorbic acid, hydroxylamine and $K_3Fe(CN)_6$(28).

Chromatography. Chromatographic methods of aluminum determination are becoming increasingly popular. Ion chromatography using a low capacity ion exchange column and conductivity detection has been successful (29). Separation of aluminum by complexation followed by column chromatography is probably most popular. Aluminum complexes of 8-hydroxyquinoline (30,31) and chelates of 2,2'-dihydroxyazobenzene (32) and N-methylfluorohydroxamic acid have been separated from other metals and then determined by spectrophotometric (30-33) or electrochemical (31) means.

Spectroscopy. Most of the above methods cannot be used to determine trace aluminum. The following section discusses methods capable of determining aluminum at low levels. Trace aluminum in biological materials can be determined by several instrumental methods not yet discussed. Spark source mass spectrometry (34), DC plasma atomic emisssion (35) and photoacoustic spectroscopy (36) are some of the rarely used techniques. X-Ray fluorescence and electron probe x-ray microanalysis have been used (37) as has direct reading emission spectroscopy (38). Proton induced x-ray emission (PIXE) for elemental analysis is also applicable if concentrations are 1 ppm or greater (39). Graphite furnace atomic absorption spectroscopy (GFAAS) is one of the more popular techniques but digestion methods and matrix modifiers can affect results.

Various matrix modifiers have been used to improve aluminum results in GFAAS (40). Rierson and Evenson (41) found Triton X-100 to be the best diluent for aluminum measurements. $Mg(NO_3)_2$ (42,43) is a common matrix modifier; recently HF and cesium

fluoride have been used (44). Fluoride allows formation of AlF_3 rather than the more refractory Al_2O_3. The advantage is that AlF_3 atomizes more rapidly or more completely than Al_2O_3 and increases sensitivity. Phosphoric acid has also been used to improve Al determinations (45). Treatment of graphite tubes with thorium nitrate has improved peak shape and allowed higher charring temperatures (46).

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is another popular method for determining trace elements. Although not as sensitive as GFAAS it has a larger linear dynamic range and multielement capabilities. Acid digestion (47,48) or dry ashing followed by melting fluxes (49,50) is often used for sample decomposition. Aluminum can be done by ICP-AES but the broad emission spectrum of calcium increases the aluminum background and raises the detection limit (37). Ward et al. (47) have determined aluminum by ICP-AES using three different sample digestion techniques. Mauras and Allain (51) have determined aluminum in blood, dialysis fluid and water. Lichte et al. (49) determined aluminum in biological materials using a dry ash/Na_2CO_3 flux sample digestion method. Kalra et al. (52) determined aluminum after microwave digestion of tree foliage. Koch et al. (53) determined aluminum in tea and coffee. All these workers used ICP-AES.

Neutron Activation Analysis. Neutron activation analysis (NAA) is also a popular method for trace element analysis. It is nondestructive and has multielement capabilities. Care must be taken to account for interferences from silicon and phosphorus. Knowledge of accurate silicon and phosphorus concentrations is necessary to obtain reliable aluminum data.

Garmestani et al. (54) and Gillmore and Goodwin (55) have determined aluminum in bones and urine using destructive NAA. The sample is digested, then the solution passed through a cation exchange resin to remove phosphorus and silicon. The aluminum is irradiated on the resin. In many cases aluminum is determined by irradiating with thermal and then epithermal neutrons and subtracting the portion of the ^{28}Al signal due to

phosphorus. Velandia and Perkons (56) have used a fast ion exchange group separation on digested heart tissue samples after irradiation. Lavi et al. (57) have used cadmium shields for epithermal irradiations. Bem and Ryan (58) have used boron carbide and Landsberger and Arendt (59) have used both. Maihara and Vasconcellos (60) and Ward and Mason (61) have used hydrated antimony pentoxide to remove sodium prior to aluminum determination. In neither case is there mention of phosphorus correction. Aluminum has also been determined in medicinal plants (62), bovine tissues (63), NIES pepperbush (64) and a variety of biological tissues (59,65).

Sample Dissolution. LeGendre and Alfrey (66) used saturated EDTA to extract aluminum from bone, muscle and brain samples. The supernatant was used directly for analysis. They found that nitric acid digestion gave erratic results. Smeyers-Verbeeke and Verbeelen (67) found that the EDTA extraction method gave consistently low results and used a brittle fracture technique (grinding at liquid nitrogen temperature) to decompose bone samples. Stevens (68) dissolved samples in tetramethyl ammonium hydroxide (TMAH). He found TMAH and acid digestion methods to be equivalent. Sullivan et al. (69) determined aluminum in various food samples by fusing the samples with sodium carbonate/sodium borate mixtures. Sodium suppresses the aluminum signal but this method allowed all forms of aluminum to be detected.

Acid digestion is the most commonly used method of sample dissolution. Mixtures of $HNO_3/HF/H_2SO_4$ (41), $HNO_3/HClO_4$ (53,70), HNO_3/H_2SO_4 (71) and HNO_3 alone (2,54) have been used. H_2O_2 has also been added to acid digestions (71). It oxidizes resistant organics and decolorizes the solution. H_2O_2 is safer and easier to use than $HClO_4$. Perchloric acid and other chloride-containing compounds were found to interfere with the Al atomic absorption signal and gave low sensitivity (72).

1.2 STANDARD REFERENCE MATERIALS

1.2.1 What are they?

A reference material (RM) is a substance for which one or more properties are established sufficiently well to calibrate a chemical analyzer or to validate a measurement process (73). An internal reference material (IRM) is developed by a laboratory for its own use. A certified reference material (CRM) is a reference material issued and certified by an organization accepted to be technically competent (73). CRMs are stable, homogeneous and well characterized reference materials prepared in quantity and having very similar matrices to test samples so as to minimize matrix effects (74). Standard reference materials (SRMs) are CRMs issued by the National Institute for Standands and Technology (NIST) in the USA.

1.2.2 Production of reference materials.

Several steps are required in the production of RMs. First of all there must be a demonstrated need for a specific type of RM. The properties of a useful RM must undergo careful consideration. The kind and level of parameters certified, the matrix and other physical characteristics, homogeneity requirements and largest acceptable uncertainties for the certified values are important considerations (75). Questions often asked here are: What is the measurement problem? Who is affected? How will the RM assist in resolving these problems? (76). When a material has been selected measurements are made to evaluate its compliance with the specifications. Since each measurement of a property involves material variability and method imprecision, homogeneity is most important (77). Homogeneity differs with the type of material and elements or properties to be certified but in each case the material must be sufficiently uniform to satisfy the end use (77). Homogeneity is becoming increasingly demanding as measurements become more precise or can be made with smaller quantities of material (78).

Homogeneity is initially tested for by rapid multielement methods. These typically include optical emission spectroscopy, X-ray fluorescence, spark source mass spectrometry and instrumental neutron activation analysis (76). Final homogeneity evaluation is made from certification data on each property or constituent (75). This requires design and execution of measurement programs so that variance of measurement and sample composition can be individually evaluated.

Certification measurements follow a quality assurance plan. This requires development of a statistical plan for sampling and measurement, selection of methodology which is reliable, maintenance of statistical control of the measurement process, and quality assessment of suitable RMs (75). Methodology can be of three types. The first is use of a definitive method. A definitive method has a valid theoretical foundation, negligible systematic errors and high precision (76). If a definitive method is used data from two or more analysts working independently are required to minimize bias. Definitive methods are not always available and the next best method is the use of two or more independent techniques. The third method of certification is use of a network of laboratories of established competence. In this case methods of proven accuracy and use of existing RMs as controls are required.

Production of RMs is preceded by a study of the suitability of the proposed materials. Only materials which have a long shelf life are used in so far as possible. RMs are also usually prepared in batches which will last several years based on the anticipated demand.

1.2.3 Use of reference materials.

RMs are designed to be used for monitoring systems that are already in a state of statistical control. RMs can also be used in method development and evaluation. Measurements on an RM may be considered to be a random sampling of the output of the measurement system and can be used to evaluate the measurement process. They may also

be used to evaluate the suitability of a proposed method for a special purpose or to determine performance characteristics (precision, accuracy and sensitivity) of methods under development. RMs are best used to demonstrate accuracy because of their known parameters.

SRMs and CRMs are widely used to assure compatible data. If laboratories can produce acceptable measurements, they can by use of SRMs be said to be intercalibrated with other laboratories and NIST (73). SRMs can be used in three cases as quality assurance (QA) materials (73). The first is when a matrix match to the test sample is possible. In this case the standard deviation of a set of sample measurements can be equated to that observed in measurement of the SRM. If the SRM has a related matrix, the test sample standard deviations may be comparable to those obtained when measuring the SRM. If matrix matches are not possible, the SRM can be used to monitor the measurement system. If use of a single SRM does not fully evaluate a measurement system several RMs may be used.

RMs can also be used to determine the precision of a method of measurement, but how well this may be transferred to real life measurements and how well potential biases are evaluated is a matter of judgement (79). They can also be used in internal quality assurance, and in the calibration of instruments, methods and standards. Standards should be appropriate and accurate. In this case RMs are ideal.

The use of control charts is another internal QA technique. They can demonstrate statistical control, monitor a measurement process and provide an estimate of uncertainty (73). Control samples should be similar to the test samples routinely analyzed and should be homogenous and stable. Here again RMs work well.

RMs can also be used in external QA. Samples for evaluation are often distributed to a laboratory by an external organization to assess a laboratory's competence. The samples distributed contain known concentrations of analyte, determined by exhaustive analysis by the laboratories of the organization, by labs in which the organization has

confidence, or by preparation of samples of known composition (80). For this purpose RMs can be excellent provided that they are not recognized as a check sample by the laboratory doing the analysis.

RMs can also be used to establish measurement traceability. Traceability means the ability to trace and implies an unbroken, identifiable, demonstrable pathway (73). Measurements have traceability to the designated standard only if scientifically rigorous evidence is produced on a continuing basis to show that the measurement process is producing measurement results for which the total measurement uncertainty relative to national or other standards is quantified (81). Traceability is the capability of reconstructing the chain of events and the assignment of a final statistically reportable total measurement uncertainty to any standard that is used in a measurement process (73). This definition stresses requirements related to quantifying measurement uncertainty and hence the quality of measurements. RMs can be used to achieve traceability.

RMs can also be used to develop secondary RMs. Here traceability is important if the secondary RMs are to be used for field measurements.

1.2.4 Kinds of reference materials.

RMs fall into three general categories (73):

a) certified chemical composition/purity standards

b) certified physical property standards and

c) engineering property standards.

Industrial materials that are analyzed for quality control of production processes make up a large fraction of all RMs. This group contains metals, all major alloy types, ores , minerals, glass, cement and ceramics (73). High purity chemicals are another important group of RMs. They are used to prepare solutions which can be used to standardize other reagents.

Clinical laboratory standards also constitute an important and rapidly growing group of RMs. There are 3 major types (82):

a) matrix material consisting of human serum, urine or animal blood with certified constituents

b) high purity organic and inorganic compounds for preparing solution calibrations or spiking matrix solutions and

c) instrument performance RMs.

Environmental RMs are necessary for reliable determination of pollutants in environmental materials. These can help determine effectiveness of pollution control measures, to assemble reliable data on emission transport or fate of pollutants and in the routine monitoring of pollutants (76). Due to the wide variety of sample types and constituents environmental RMs are usually high priority sample types or generic materials that are widely applicable (73). However, several natural matrix RMs certified for most of the inorganic and some organic constituents are available. These include biological matrix samples, urban particulate matter, river and marine sediments, and industrial hygiene materials.

Physical property standards reflect the many kinds of measurements made in testing laboratories (75). They are useful for measurement of temperature, melting points, fineness of powders, and so on. Radioactivity standards are found in this category.

1.2.5 Sources of reference materials.

NIST has pioneered and continues to be the leader in the development of RMs. They produce all the types discussed above, and provide them as SRMs. The total number of SRMs available is approximately 1000.

The National Research Council of Canada has for some years operated a Marine Analytical Chemistry Standards Program which produces RMs for marine studies. These RMs, which include water, biological and sediment materials, are mostly certified for

inorganic elements, but some organic constituents have been included. The latest RM, LUTS-1, is the only RM with an unaltered matrix. It consists of lobster hepatopancreas homogenized with water and sold as a slurry.

The Canada Centre for Mining and Energy Technology has a certified reference material program. Their compositional RMs are for use in analytical laboratories associated with mining and metallurgy and the earth sciences. Approximately 50 RMs are divided into three categories (83): a) ferrous spectrographic standards, b) copper and copper alloys, and c) Canadian metal bearing ores. The last group is the largest, owing to the large demand for certified reference ores that are typical of major deposits in Canada (83).

Environment Canada has an aquatic QA program which produces sediment RMs. Some of them are certified for organic and inorganic constituents. The Community Bureau of Reference in Europe produces about 400 CRMs. They include environmental, food and agriculture, biomedical and industrial RMs (84). The National Institute for Environmental Studies in Japan produces environmental RMs. Presently about 10 biological and sediment RMs are available (85). The U.S. Geological Survey and the International Atomic Energy Agency also produce RMs. Thus it can be seen that many organizations world wide produce RMs. The above agencies are representative. A complete list of RMs and their suppliers is available from the International Standards Organization (86).

1.3 RESEARCH OBJECTIVES

The main focus of this work was a comparison of methods for the determination of aluminum in a variety of agricultural materials. Due to the difficulty of obtaining accurate aluminum values for trace levels in biological matrices, we decided to select three promising methods for comparison. The methods needed to be rapid and capable of detecting trace amounts of aluminum. After consideration of these points and the instrumentation available, the techniques chosen were graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-

AES) and instrumental neutron activation analysis (INAA). For aluminum determinations by INAA it is necessary to know the phosphorus and silicon content. Since these values were not known, they also had to be determined to correct the INAA values for aluminum.

The matrices studied were potential RM's under development by Dr. Milan Ihnat of Agriculture Canada, and consisted of finely ground bran, flour, gluten, meat, starch, cellulose, whole egg powder, whole milk powder, corn stalk and corn kernel. These materials have all been sterilized to prevent decomposition by microbiological growth, and have been carefully homogenized. The corn kernel and corn stalk materials are presently available from the U.S. National Institute for Science and Technology, who are serving as distributors; the others are being held pending sufficient analytical data to allow release.

CHAPTER 2

DETERMINATION OF ALUMINUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

2.1 INTRODUCTION

Atomic absorption spectroscopy (AAS) is a highly specific means of elemental analysis based on the selective absorption of line radiation by atomic species in the vapour phase (87). The light source from which absorption takes place is usually a hollow cathode lamp. The lamp produces the emission spectrum of the element of interest. Many advantages of AAS can be directly or indirectly attributed to the narrow widths of the resonance lines (88).

Production of free neutral atoms from the sample by thermal dissociation takes place in a flame or in an electrothermal (ET) atomizer. The greatest advantage of ET atomization arises from retention of a large portion of the atomized analyte element in the observation zone for a finite period of time (89,90). This results in greater sensitivity and lower detection limits, often 1000 times better than using a flame (89).

Other advantages of ET atomization include a small sample volume (89) and the possibility of analyzing solid samples (89,90). Over the years AAS using ET atomization has had several developments which have improved precision, sensitivity and reliability. These include the introduction of autosamplers, improved gas flow programming and better temperature control during the ashing and atomization stages. Pyrolytically coated graphite tubes, the introduction of platforms within the tubes and the introduction of Zeeman (91) and Smith-Heiftje (92) background correction, along with fast data evaluation, have also improved the usefulness of ETAAS.

The typical atomization furnace has a three step program. The first step, drying, is used to evaporate solvent from the 10 to 100 µL sample solutions injected into the furnace.

Solvent evaporation should occur in a slow controlled manner to prevent loss by spitting or boiling of the sample (89).

The second step, ashing, is most important. The success of any ETAAS analysis depends in a major way on thorough destruction of the matrix. Since optimum destruction depends on the matrix itself (89), selection of correct conditions is important. Too high an ashing temperature will result in loss of analyte before the atomization stage.

In the last step, atomization, the remaining analyte is heated rapidly to produce free neutral atoms. Each element has a characteristic ashing temperature and residence time in the furnace.

2.2 EXPERIMENTAL

2.2.1 Apparatus

Atomic absorption measurements of aluminum were made on a microprocessor controlled spectrophotometer (Perkin Elmer Model 5000). A deuterium hollow cathode lamp (HCL) was used for background correction. An HGA 2200 furnace with 3 stage programming was used for atomization of the sample and an AS-1 autosampler with fixed 20 µL injection was used to inject samples into the furnace. Pyrolytically coated graphite tubes with solid pyrolytic graphite platforms were used (Perkin Elmer part numbers 0290-1822 and B012-1091). Operating conditions were as follows: wavelength 308.2 nm; integration time 6 sec; slit width 0.7 nm; drying temperature and time 120°C, 50 sec; ashing temperature and time 1400°C,30 sec; atomization temperature and time 2550°C, 6 sec; hollow cathode lamp current, 12 mA. The argon purge gas flow was continued using the normal (40 mL/min) setting for the first 6 seconds of atomization. Peak areas were recorded on a Perkin Elmer PRS-10 printer sequencer.

The microwave oven used in this work was a 700 W Sears Kenmore Model 87760. It has a timing cycle ranging from 1 sec to 100 min in 1 sec intervals. The heating cycle ranges from 0% to 100% power in 1% intervals and is based on fraction of total power

output. The oven can accomodate 8 digestion vessels with relatively even heating. The screw-cap, wide-mouth digestion vessels have a capacity of 60-mL and are made of Teflon PFA (Savillex Corp., Minnetonka, Minnesota). A Litton Ware microwave turntable was used in the oven to provide more even energy distribution to the samples.

Working standards were prepared by pipetting appropriate volumes of a 1000 µg/mL Al stock solution (Fisher Scientific Certified Atomic Absorption Standard) and diluting to 50 mL. All solutions were stored in polyethylene volumetric flasks (Nalgene Labware).

Standard reference materials used were NIST 1575 Pine Needles, NIST 1577a Bovine Liver and NRC TORT-1 lobster hepatopancreas.

2.2.2 Sample Drying and Mixing

Four bottles each of Bran, Flour, Gluten, Whole Egg Powder, Whole Milk Powder, Meat, Starch and Cellulose were obtained from Agriculture Canada, Ottawa through Dr. Milan Ihnat. One bottle each of Corn Kernel and Corn Stalk were purchased from the National Institute for Science and Technology, Gaithersburg, M.D., USA 20899. All samples were tumbled end-over-end for at least 2 hours. This time was found adequate in past work on a variety of reference materials. After tumbling, about 5-g portions were transferred to clean, dry glass weighing bottles and dried at 85°C for 4 hours.

2.2.3 Closed-vessel Microwave Acid Digestion Using HNO_3 and HF

Approximately 250-mg samples of Bran, Flour, Gluten, Starch, Cellulose, Corn Kernel and Corn Stalk were weighed into 60-mL Savillex digestion vessels, 2 mL double sub-boiling distilled in quartz HNO_3 (Seastar Chemicals, Sidney, B.C., Canada) and 0.5 mL HF (Fisher Scientific) were added and the lids tightened with the wrenches provided with the vessels. The vessels were placed on the turntable inside the microwave oven and were heated at 100% power for 40 sec. After cooling the vessels were opened to allow

release of nitrogen oxides formed during the heating step. This was followed by a second heating step of 60 sec at 100% power. Again the vessels were cooled and opened. A third heating step involved heating at 100% power for 90 sec followed by 5 min at 10% power. After cooling for about 10 minutes in the air, the contents were transferred to 30-mL Teflon bottles (Nalgene Labware) which contained 0.465g solid H_3BO_3. The amount of H_3BO_3 used was determined by the amount of HF used since its purpose is to complex fluoride as fluoroborate. Bran, Starch and Cellulose solutions were diluted to 11 g, Flour, Gluten and Corn Kernel to 15 g. The final volume was determined for each by measuring the density of a 1-mL portion of the solution. The Corn Stalk solution was diluted to 100 mL in polyethylene volumetric flasks.

2.2.4 Closed-vessel Microwave Acid Digestion Using HNO_3

Approximately 250 mg samples of Whole Egg Powder, Whole Milk Powder and Meat were weighed into 60-mL Savillex digestion vessels and 3 mL of HNO_3 were added. The lids were tightened and the vessels were placed on the turntable in the oven and heated for 40 sec at 100% power. After cooling for 10 minutes in the air the vessels were vented. The samples were then heated for 60 sec at 100% power. Again, after cooling and venting the vessels, the samples were heated for 90 sec at 100% power followed by 5 min at 10% power. After cooling, the Whole Egg Powder samples were transferred to 100-mL polyethylene volumetric flasks and diluted to 100 mL. Meat and Whole Milk Powder samples were transferred to 30-mL Teflon bottles and diluted to 11 g. The final volume was determined for each by weighing a 1-mL portion of the solution.

2.2.5 Standard Addition Procedure and Atomic Absorption Measurements

For Flour, Gluten, Whole Egg Powder and Corn Stalk four 1-mL aliquots of the resultant solutions were pipetted into four preweighed 10-mL Teflon FEP Oak Ridge centrifuge tubes (Nalgene Labware). An Eppendorf 100 to 1000 µL micropipet was used

to transfer 1 mL of 0.547 M $Mg(NO_3)_2$ into the tubes followed by additions of typically 0, 200, 400, and 600 µL of a standard 1 µg/mL aluminum nitrate solution. Deionized water was used to dilute all solutions to about 10 g. The final weight of solution was determined by weighing the tube after dilution. The value of the aluminum concentration was determined by least squares calculations on the standard additions plot using equation 2.1 as given in Harris and Kratochvil (93).

$$V_c = \frac{(\Sigma A)(\Sigma V^2) - [\Sigma(AV)](\Sigma V)}{n[\Sigma(AV)] - (\Sigma A)(\Sigma V)}$$

The standard deviation of the intercept is calculated by

$$s^2 = \frac{\Sigma d^2 \, \Sigma(V+Vc)^2}{n-2 \, (\Sigma A_{calc})^2} \Big/ \frac{n\Sigma(V+Vc)^2}{[\Sigma(V+Vc)]^2} - 1$$

where ΣA is the sum of the absorbance readings; ΣV is the sum of volumes of standard Al added; V_c is the horizontal axis intercept; n is the number of solutions read; A_{calc} is the calculated absorbance of a solution, and d is the difference between A and A_{calc} for each point.

For Bran, Meat, Starch, Cellulose and Corn Kernel 2 mL of sample solution was used. The solutions were then diluted and the concentrations determined as above.

For Whole Milk Powder samples the standard addition procedure was not used. The direct readings of sample solutions diluted 1:1 with 0.5 M $Mg(NO_3)_2$ were compared to a calibration curve prepared in 30% HNO_3.

2.3 RESULTS AND DISCUSSION

Results of analyses of the three reference materials used in this work are shown in Table 2.4. The values for TORT-1 agree well with work done earlier in this laboratory, and fall within the approximate value given by NRC Canada (94). Pine Needles values

tend to be slightly lower than the certified value but are not out of range of those found in the literature for this material (4). The value for Bovine Liver is in good agreement with the approximate value; this material is not certified for aluminum because of lack of agreement among methods. The agreement in general indicates that the analytical methodology was in a state of statistical control.

Results for the aluminum analyses are shown in Tables 2.1-2.3. The uncertainty behind each value is the uncertainty in the least squares intercept for the standard additions procedure. The uncertainty of the averages of each bottle and the overall average are one standard deviation for all measurements. The uncertainties in the SRM's and in the Canadian CRM's are tolerance limits, that is, that 95% of the measurements will fall within the given range 95% of the time. The $Mg(NO_3)_2$ used in the measurement step allows the formation of MgO during the char step to reduce the volatility of aluminum until the higher atomization temperature is reached (95). Whole Milk Powder was found to have a very low Al content and much scatter was seen in the values. Least squares was not used for Whole Milk Powder because the sample size that could be dissolved was limited and preparation of standard additions would require further dilution of the sample, thereby further decreasing the concentration of aluminum in the sample solution. The limitation on determining Al in this material comes from the limit on size of sample that could be dissolved in the bomb. Samples greater than 0.25 g produce very large amounts of nitrogen oxides and were dangerous because of possible bomb explosion. Although it is recommended (96) that unvented vessels not be used in the microwave, these vessels can be used if care is taken to choose a digestion scheme that avoids extreme pressure buildup. We used frequent venting to prevent a buildup of gas pressure in the digestion vessels.

The data were tested for differences in within vs. between bottle homogeneity by a one-way analysis of variance. Prior to running of the ANOVA program the data were tested by the Dean and Dixon Q test (97) and values falling outside the Dean and Dixon criteria at the 90% confidence level were deleted from the data set. The statistical analyses

were performed on an Apple Macintosh computer using the statistical package Statworks by Data Metrics Inc. ANOVA and descriptive statistics on the data are given in Appendix 1.

The table F ratio, which expresses the relative magnitude of the between-bottle to within-bottle homogeneity, is 3.49, 3.34 and 3.29 for 3 between bottle and 12,14 and 15 within bottle degrees of freedom (98) at the 95% confidence level. The F values of the agricultural materials are given in Table 2.5. All of the F ratios fall below the table values at the 95% confidence levels, indicating that the materials are homogeneous at the 250 mg sample size. No ANOVA was done on the Whole Milk Powder because of the large scatter in the values obtained.

An important part of determining sample homogeneity is differentiation of measurement and subsampling uncertainty. If measurement uncertainty is small the precision with which the subsampling uncertainty can be determined will be high. Table 2.5 lists in column 4 the standard deviation in the measurement step, s_m. The average of the s_m values for the standard additions was used as the s_m value for the purpose of this calculation. From these values the standard deviation in the subsampling step, s_s, can be obtained (99) by

$$s_s = (s_o^2 - s_m^2)^{1/2} \qquad (2.2)$$

From the values for s_s calculated by equation 2.2 and listed in Table 2.5, it can be seen that the fraction of the overall standard deviation contributed by the subsampling step is very large in each case. If the value of s_m is larger than the average, s_s becomes smaller and the fraction of s_o due to s_s becomes somewhat smaller. However it is still clear that the largest part of the overall standard deviation in all the materials studied here is due to sampling. We conclude that even though the subsampling step contributes the largest uncertainty to the results, the F ratios are still below table values, indicating that the materials provided by Agriculture Canada are homogeneous at the sample sizes used.

Table 2.1 Atomic Absorption Results for Al in Agricultural Materials in μg/g.

Bottle No.	FLOUR 187	Bottle No.	GLUTEN 184	Bottle No.	BRAN 186
488	13.77 ± 0.41	532	11.35 ± 0.46	312	2.91 ± 0.10 *
	16.90 ± 0.13 *		12.22 ± 0.44		1.53 ± 0.09
	13.93 ± 0.06		10.64 ± 0.50		1.39 ± 0.05
	13.24 ± 0.45		10.21 ± 0.12		1.22 ± 0.08
Average	13.65 ± 0.36	Average	11.10 ± 0.88	Average	1.38 ± 0.08
640	13.46 ± 0.57	639	10.33 ± 0.31	390	1.50 ± 0.17
	13.98 ± 0.34		10.39 ± 0.23		1.09 ± 0.08
	11.23 ± 0.26		11.57 ± 0.31		2.02 ± 0.07
	12.64 ± 0.42		11.31 ± 0.28		1.23 ± 0.06
Average	12.83 ± 1.20	Average	10.90 ± 0.63	Average	1.46 ± 0.41
935	11.39 ± 0.80	1288	11.86 ± 0.18	927	1.40 ± 0.02
	14.00 ± 0.16		12.33 ± 0.25		1.15 ± 0.07
	14.62 ± 0.26		11.88 ± 0.26		1.06 ± 0.07
	12.50 ± 0.17		8.29 ± 0.18 *		1.53 ± 0.06
					1.83 ± 0.07
Average	13.13 ± 1.46	Average	12.02 ± 0.26	Average	1.39 ± 0.31
971	16.25 ± 0.59	1328	10.29 ± 0.33	1428	1.33 ± 0.04
	14.32 ± 0.22		12.74 ± 0.53		1.02 ± 0.06
	12.70 ± 0.18		9.90 ± 0.16		1.48 ± 0.05
	11.43 ± 0.26		9.72 ± 0.13		1.52 ± 0.15
	12.88 ± 0.16				
	12.80 ± 0.22				
Average	13.40 ± 1.67	Average	10.66 ± 1.40	Average	1.34 ± 0.23
Overall Ave	13.24 ± 1.28		11.16 ± 0.97		1.39 ± 0.27

* Rejected by Q-test

Table 2.2 Atomic Absorption Results for Al in Agricultural Materials in µg/g.

Bottle No.	WHOLE EGG POWDER 183	Bottle No.	MEAT 136	Bottle No.	WHOLE MILK POWDER 188
329	549 ± 19	57	0.989 ± 0.054	295	0.232 ± 0.042
	482 ± 8		0.885 ± 0.066		0.226 ± 0.028
	494 ± 7		1.63 ± 0.060		0.918 ± 0.054
	530 ± 13		0.669 ± 0.070		0.356 ± 0.069
			1.07 ± 0.080		
Average	514 ± 31	Average	1.05 ± 0.360		**
512	462 ± 7	422	0.678 ± 0.056	997	0.314 ± 0.048
	435 ± 6		1.30 ± 0.060		0.585 ± 0.104
	546 ± 9		0.728 ± 0.051		0.628 ± 0.001
	443 ± 12		1.21 ± 0.090		
			0.822 ± 0.075		
Average	472 ± 51	Average	0.948 ± 0.287		**
751	484 ± 11	1817	0.906 ± 0.073	1234	0.317 ± 0.034
	544 ± 9		1.14 ± 0.050		0.833 ± 0.067
	526 ± 10		1.03 ± 0.080		0.296 ± 0.037
	445 ± 12		1.09 ± 0.060		
Average	500 ± 44	Average	1.04 ± 0.100		**
1930	497 ± 9	3019	1.42 ± 0.030	1262	0.259 ± 0.030
	543 ± 12		0.824 ± 0.037		0.333 ± 0.049
	498 ± 7		0.981 ± 0.083		0.402 ± 0.039
	513 ± 12		0.605 ± 0.045		
			0.682 ± 0.060		
Average	513 ± 21	Average	0.902 ± 0.323		**
Overall Ave	499 ± 39		0.982 ± 0.275		0.441 ± 0.240

	CORN KERNEL		CORN STALK
	4.00 ± 0.11		80.18 ± 1.46
	3.96 ± 0.11		70.19 ± 0.85
	3.88 ± 0.12		76.10 ± 1.07
	3.66 ± 0.10		69.58 ± 2.44
	3.50 ± 0.06		78.03 ± 2.02
	4.44 ± 0.12		79.92 ± 0.71
Average	3.91 ± 0.32	Average	75.67 ± 4.72

** Because of scatter, calculation of average was not considered appropriate for individual bottles.

Table 2.3 Atomic Absorption Results for Al in Agricultural Materials in μg/g.

Bottle No.	CELLULOSE 189	Bottle No.	STARCH 162
479	3.65 ± 0.10	140	1.80 ± 0.06
	3.56 ± 0.10		2.30 ± 0.12
	4.34 ± 0.08		2.76 ± 0.06
	3.06 ± 0.05		2.35 ± 0.06
Average	3.65 ± 0.53	Average	2.30 ± 0.39
497	3.63 ± 0.07	412	2.64 ± 0.04
	3.11 ± 0.08		1.45 ± 0.06
	3.23 ± 0.13		1.56 ± 0.08
	4.94 ± 0.09		2.65 ± 0.06
Average	3.73 ± 0.84	Average	2.08 ± 0.66
662	3.87 ± 0.04	869	1.43 ± 0.08
	4.25 ± 0.12		1.79 ± 0.12
	4.45 ± 0.03		2.07 ± 0.08
	4.43 ± 0.14		2.21 ± 0.08
Average	4.20 ± 0.24	Average	1.88 ± 0.34
1791	2.88 ± 0.03	1591	3.18 ± 0.07
	3.36 ± 0.11		2.90 ± 0.10
	3.11 ± 0.07		2.57 ± 0.16
	4.73 ± 0.14		1.62 ± 0.06
Average	3.52 ± 0.83	Average	2.57 ± 0.68
Overall Ave	3.79 ± 0.66		2.20 ± 0.55

Table 2.4 Atomic Absorption Results for Al in Standard Reference Materials in μg/g.

	TORT-1	Pine Needles	Bovine Liver
	42.68 ± 1.36	522 ± 2	1.38 ± 0.08
	47.55 ± 1.39	536 ± 2	2.42 ± 0.15
	37.29 ± 0.96	522 ± 4	1.23 ± 0.06
	38.28 ± 0.10	520 ± 10	2.21 ± 0.13
	44.78 ± 1.07	500 ± 15	1.13 ± 0.04
	43.19 ± 1.12		1.43 ± 0.04
			1.91 ± 0.19
Overall Ave	42.30 ± 3.90	520 ± 13	1.67 ± 0.51
Cert. Value	(42 ± 2)	545 ± 30	(2)

Table 2.5 Standard Deviation in μg Al/g due to Sampling of Agricultural Materials by Atomic Absorption Spectroscopy.

Sample	Calculated F Ratio	s_o[c]	s_m[c]	s_s[c]	Fraction of s_o due to s_s
Flour 187	0.239	1.51	0.31	1.48	0.96
Gluten 184	0.102	1.17	0.29	1.13	0.93
Bran 186	0.113	0.27	0.07	0.26	0.93
Egg Powder 183	1.036	39	10	38	0.95
Milk Powder 188	a	0.24	0.05	0.23	0.92
Meat 136	0.286	0.28	0.06	0.27	0.93
Starch 162	1.216	0.55	0.08	0.54	0.96
Cellulose 189	0.940	0.66	0.09	0.65	0.97
Corn Kernel	b	0.32	0.10	0.30	0.88
Corn Stalk	b	4.72	1.42	4.50	0.91

a Not calculated since measurements are near detection limit.

b Only a single bottle of material available, so s_s could not be calculated as for the other materials.

c s_o, s_m and s_s are the overall, measurement and subsampling standard deviations.

CHAPTER 3

DETERMINATION OF ALUMINUM AND SILICON BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

3.1 INTRODUCTION

The inductively coupled plasma instrument consists of an induction coil wrapped around a quartz tube. The coils generate magnetic fields which create a circulating current in a conductor. The conductor is argon gas which is made conductive by heating. The plasma discharge is started by applying a Tesla coil discharge to the argon (100).

Temperatures inside the plasma reach about 10000 K (101). By use of a higher frequency oscillation in the power source a doughnut shaped plasma is formed . This has a lower temperature (7000 K) and lower resistance to injection of sample. High temperatures and long residence times lead to high if not total atomization of analyte species (101). The temperature and residence times are twice those experienced by samples in a nitrous oxide-acetylene flame. Atoms flow downstream in a narrow cylindrical channel inside the plasma (102). This allows the viewing field to be filled so that emitted radiation is used effectively. At the normal height of observation, which is about 1 to 3 cm above the induction coil, the channel has a uniform temperature profile and an optically thin window. This allows the instrument to accomodate a large range of emission intensities and a large linear dynamic range (102).

Solute vaporization interferences are reduced because of the high temperature, long residence times and inert environment provided by the plasma (103). Most interelement or matrix effects will also be overcome. Further, ICP-AES is suited to simultaneous multielement determinations because one set of parameters is usually satisfactory for all metals.

In summary the advantages of ICP-AES are: multielement capability; high stability; high sensitivity; and minimal chemical interferences. ICP-AES also has some

disadvantages: spectral background may be a problem, and ionization interferences can occur but they may be corrected by addition of an appropriate spectroscopic buffer.

3.2 EXPERIMENTAL

3.2.1 Apparatus

The ICP measurements were obtained on a Leco PLASMARRAY ICP spectrometer. This is the first commercial ICP that uses a photodiode array detector and is capable of multielement analysis with simultaneous background correction.

The spectrometer consists of a preselection polychromator (PSP), recombination optics and an echelle spectrometer. The PSP consists of the entrance slit , a concave grating and a mask. The mask allows only desired spectral information to pass through to the rest of the spectrometer. Flexibility of changing from one set of analytical lines to another quickly and reproducibly is a great advantage. In this work a multielement mask was used because a mask for aluminum only was not available.

The recombination optics are a mirror and a second grating which cancels dispersion produced by the first grating. The final stage is a one meter echelle spectrometer composed of an echelle grating, a camera mirror and the photodiode array detector.

The data was acquired by a Leco 386 instrument computer with a 16 MHz 80386 central processor and as 80387 numeric co-processor.

The plasma had an incident power of 1.9 kW and was run at 27.1 MHz with argon flows as follows: plasma 15 L/min.; auxiliary 0.8 L/min.; nebulizer 0.5 L/min. The nebulizer flow rate was 1.0 mL/min. and the nebulizer pressure was 30 psi argon. The analysis lines used were 251.6 nm for silicon and 309.3 nm for aluminum.

3.2.2 Sample Drying and Mixing

Four bottles each of Bran, Flour, Gluten, Whole Egg Powder, Whole Milk Powder, Meat, Starch and Cellulose were obtained from Dr. Milan Ihnat of Agriculture

Canada, Ottawa. One bottles each of Corn Kernel and Corn Stalk were purchased from the U.S. National Institute for Science and Technology. All samples were tumbled end-over-end for at least 2 hours. After tumbling, about 5 g portions were transferred to clean, dry glass weighing bottles and dried at 85°C for 4 hours.

3.2.3 Sample Dissolution

Approximately 500 mg of sample was weighed on a Mettler balance to the nearest 0.1 mg into Savillex 60-mL digestion vessels and 5 mL of aqua regia and 2 mL of HF were added. The vessels were capped and placed on a Littonware microwave turntable in a Kenmore microwave oven. The samples were heated at 50% power for 18 minutes and at 75% power for 5 minutes. Due to the large sample size the vessels were vented after 4, 7, and 18 minutes. The Flour, Starch and Corn Kernel were completely digested after this treatment but the other samples required an additional 9 minutes at 75% power. After cooling, 3 drops of 30% H_2O_2 was added and the vessels were placed on a sand bath at 100°C until bubbles were no longer visible. The samples were added to 0.93 g of H_3BO_3 and diluted to 15 g.

Standards were prepared from Spex 1000 ppm Si and Al standards with the same amount of aqua regia, HF and H_3BO_3 as the samples.

3.3 RESULTS AND DISCUSSION

The aluminum signal was most intense at 309.3 nm and therefore this line was used. Standards gave fairly reproducible intensities although background was high. Samples generally had aluminum levels that were too low to be quantitated. Whole Egg Powder was the only sample that had an aluminum concentration high enough to give reproducible results on replicate measurements of a given sample. However, no values are given because of the scatter that was present in the measurements between samples. Clearly this material is not homogeneous for aluminum. In general the sample size of all

the materials studied was limited to 0.5 g because of excessive pressure buildup in the digestion vessels. With sample sizes of 2 g it might have been possible to get reproducible results.

For the silicon analyses no results could be obtained for standards or samples. Silicon is very difficult to determine because of its refractory nature. Standards gave about the same peak intensities regardless of concentration. All samples also gave intensities that were similar to the standards. Since there was no distinction between solutions, it was decided that the silicon concentrations could not be obtained with this instrument under the conditions studied.

CHAPTER 4

DETERMINATION OF ALUMINUM BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

4.1. INTRODUCTION

Stable nuclei can undergo several nuclear changes when bombarded by neutrons. One reaction used in activation analysis is the neutron, gamma (n,γ) reaction, exemplified by

$$^{75}_{33}As + ^{1}n \rightarrow ^{76}_{33}As + ^{0}\gamma$$

In this example a neutron is captured by the target atom and one or more gamma rays are emitted immediately (prompt gamma emission). Since there is no change in atomic number the target atom retains its chemical identity. The (n,γ) reaction usually involves absorption of a thermal neutron. Thermal neutrons have energies of about 0.025 eV.

The (n,p) reaction requires neutrons with energies high enough to cause a proton to be released. The atomic number is reduced by one and the target atom is converted into a different element. An example is

$$^{32}_{16}S\ (n,p)\ ^{32}_{15}P$$

The (n,α) reaction requires high energy neutrons. An alpha particle (helium nucleus) is emitted and the atomic number is reduced by two.

$$^{27}_{13}Al\ (n,\alpha)\ ^{24}_{11}Na$$

Most activation analysis involves measurement of gamma rays from decaying radionuclides produced by one of the above reactions. The activity induced in a sample depends on the amount of target element, cross section of the target element, irradiation flux, irradiation time and the decay characteristics of the radionuclide formed (105). The cross section (σ) is a measure of the probability that the target element will react with the bombarding

neutron. The irradiation flux (ϕ) is the density of bombarding neutrons expressed as neutrons per square centimeter per second.

The final activity in a sample can be expressed as (105):

$$A = N\sigma\phi\,(1-e^{-\lambda t})$$

where A = induced activity at the end of irradiation

N = number of target atoms present

t = irradiation time

λ = decay constant of product nuclide and

$(1-e^{-\lambda t})$ = saturation factor.

The decay constant is expressed as (105):

$$\lambda = \frac{\ln 2}{T_{1/2}}$$

where $T_{1/2}$ is the half life of the product nuclide. As the irradiation time becomes large compared to $T_{1/2}$ the saturation factor approaches 1. Because the rate of growth of activity decreases with increasing activity the useful irradiation time is limited to about one half life (105). The sensitivity of determination for an element depends on the same factors as the activity but also depends on the efficiency of the detector and on whether or not the decay of the product nuclide is easily detected (105).

Neutron activation analysis has several advantages. The first of these is high sensitivity for many elements. NAA is excellent for multielement analysis and has the capacity for high sample throughput. Often little sample preparation is required and the irradiated material is for practical purposes essentially unaltered. (Though it may be necessary to allow time for radiation emissions to decay to safe levels before handling.)

4.2 SLOWPOKE FACILITY

The SLOWPOKE II reactor is a small pool type reactor developed by Atomic Energy of Canada Ltd. The SLOWPOKE II consists of a reactor, pool, control console and irradiation and service systems. A schematic diagram is shown in Figure 4.1.

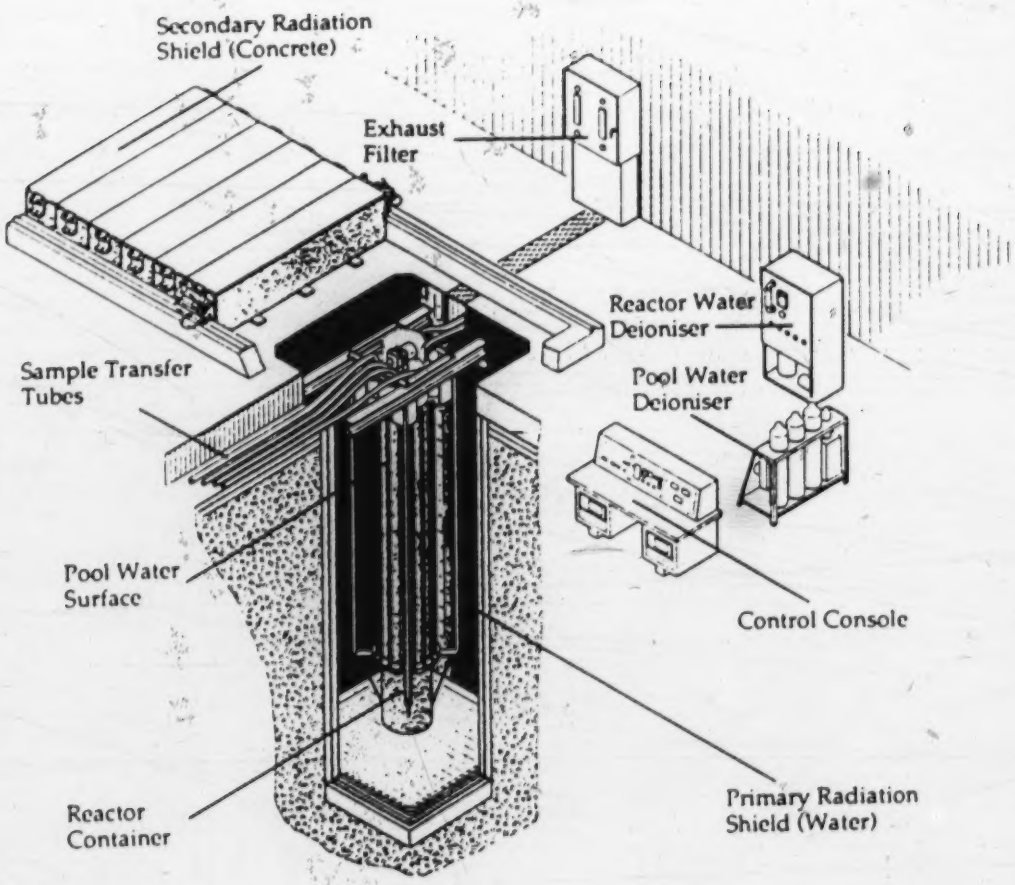

Figure 4.1 University of Alberta SLOWPOKE -II Reactor Facility (106)

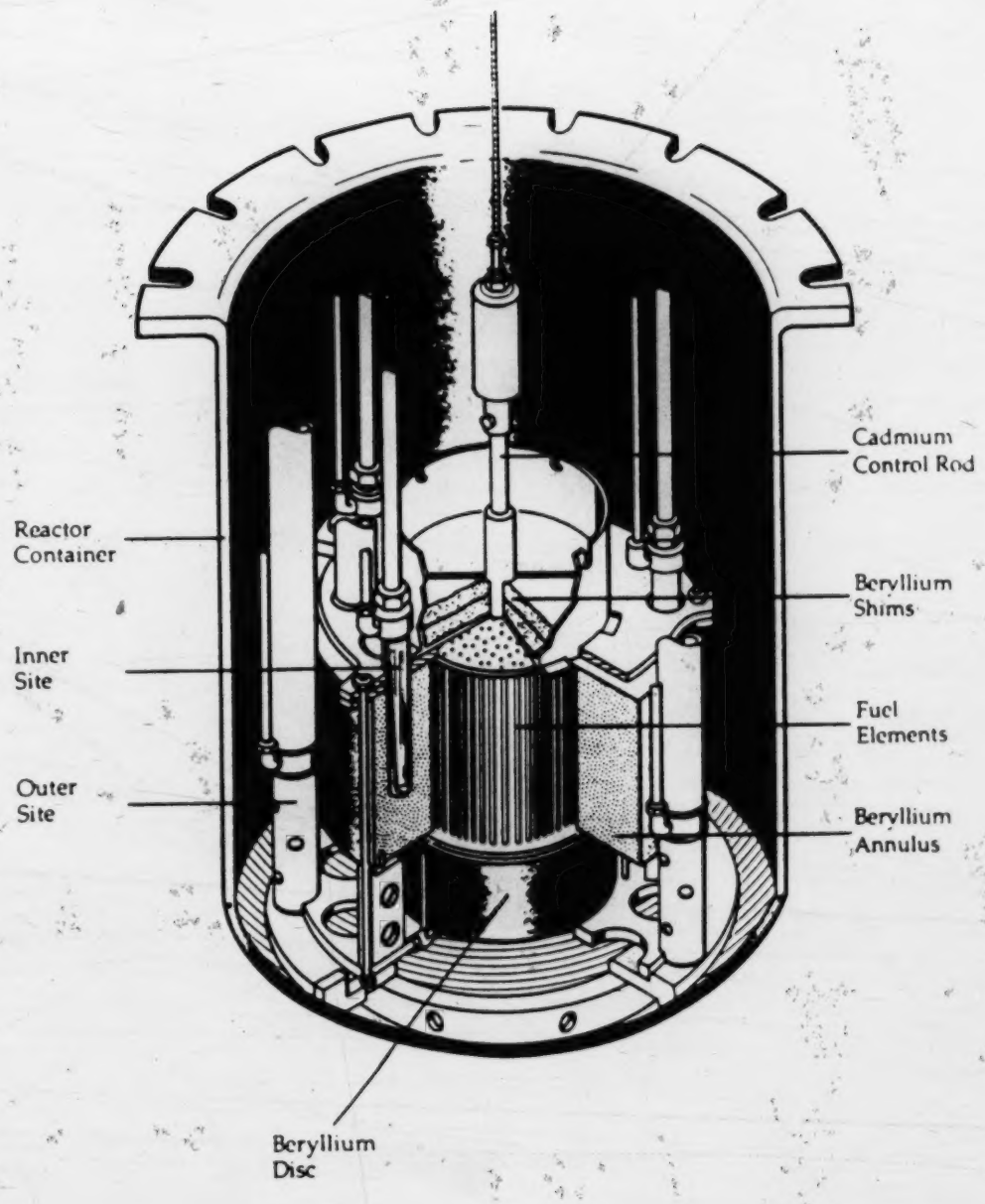

Figure 4.2 Cut-Away View of the Reactor Core (106)

The reactor core is shown in Figure 4.2. Included in the reactor are the core, beryllium reflectors, control rod and drive, neutron detector, thermocouple, five inner irradiation sites and one outer irradiation site.

The core consists of 297 fuel elements made of an Al-U alloy in which the uranium has been enriched to 93% ^{235}U (107). The small mass of uranium, only 850 g, and the negative temperature coefficient of reactivity are important features of the SLOWPOKE II. The amount of ^{235}U contained in the core is much less than the critical mass necessary to support a self sustaining nuclear reaction (107). This needed neutron flux is provided by beryllium reflectors. The beryllium reflectors reduce neutron loss to the surroundings, thereby reducing ^{235}U consumption, and also maintain an elevated thermal neutron flux in comparison to the fissile power available. The beryllium annulus and beryllium disk are 100 mm thick (107). The top beryllium shims are a few millimeters thick and additional shims can be added to compensate for fuel burn up.

A cadmium control rod moves in the centre of the fuel cage and controls the flux by neutron absorption. The flux level is measured by a neutron detector, and is normally maintained between $0.5x10^{11}$ and $1x10^{12}$ neutrons per square centimeter per second during operation (107). A thermocouple monitors the temperature of the reactor water. Deionized water is used in the reactor for moderation and cooling as well as in the pool as a primary shield. The pool water is treated by ion exchange to control contamination and is cooled by water flowing through a panel heat exchanger.

The sample irradiation system consists of polyethylene irradiation tubes and irradiation controllers. The inner irradiation sites are sample tubes which run into the surrounding beryllium reflector while the outer site is in the water outside the core. Samples are pneumatically transferred by air pressure to and from the core in polyethylene containers called rabbits.

The control console consists of a reactor control system, radiation monitoring system readouts and a service panel to monitor auxiliary systems. Additional service

systems include ion exchange purification and cooling for the pool water and a gas purging facility to prevent hydrogen build up in the reactor (107).

4.3 CORRECTIONS TO ALUMINUM COUNTS

The measurement of aluminum using the 1779 keV photopeak of ^{28}Al by the reaction $^{27}Al\ (n,\gamma)^{28}Al$ suffers from two major interferences. Phosphorus undergoes reaction with fast neutrons to produce ^{28}Al via the reaction $^{31}P\ (n,\alpha)^{28}Al$. The interference factor has been determined (108) previously. The mass of phosphorus that produces activity equivalent to 1 μg of Al irradiated and analyzed under identical conditions is determined by irradiating and counting phosphorus and aluminum standards. An interference factor value of 668 ± 30 μg P/g Al will be used here. This interference factor remains the same regardless of the flux and irradiation time used, provided the thermal to fast neutron ratio remains the same. Using inner sites of the reactor, this ratio is 16.9:1. The correction is determined by dividing the phosphorus content by the interference factor. This will give an aluminum value which can then be subtracted from the total aluminum determined. The concentration of phosphorus causes concern if it is ten times higher than the concentration of aluminum. In most biological materials the phosphorus to aluminum ratio is larger than 10 (109).

A similar correction can be made for the $^{28}Si\ (n,p)^{28}Al$ interference reaction. This interference factor, which was also determined previously, is 192 μg Si/g Al (108). The concentration of silicon also becomes a concern if it is ten times higher than the aluminum concentration. This is not generally the case in biological materials (109) but if the silicon is not known there is a measure of uncertainty in assuming that no interference is present.

4.4 EXPERIMENTAL

4.4.1 Sample Preparation

Four bottles each of Bran, Flour, Gluten, Whole Egg Powder, Whole Milk Powder, Meat, Starch and Cellulose were obtained from Agriculture Canada, Ottawa. One bottles each of Corn Kernel and Corn Stalk were purchased from the U.S. National Institute for Science and Technology. All samples were tumbled end-over-end for at least 2 hours. After tumbling, about 5 g portions were weighed to 0.1 mg, transferred to clean, dry glass weighing bottles and dried at 85°C for 4 hours.

After drying the samples were packed into clean irradiation vials. The vials were cleaned by soaking in Contrad 70 for 4 hours followed by several distilled water rinses. The vials were then soaked in 95% ethanol for 4 hours and allowed to air dry.

One gram of Flour and Gluten and 300 mg of Corn Stalk were packed into small irradiation vials. For Whole Egg Powder the small vials were partially filled with melted paraffin and then cooled before 100 mg of sample was added and the vial filled with paraffin pellets. The small irradiation vials were placed in large vials and the large vials were packed with paraffin pellets to prevent movement of the inner vial. About 1.5 g of Cellulose, 2 g of Starch, Bran, Corn Kernel, Meat and Whole Milk Powder were packed directly into large vials. The vials were then filled with paraffin pellets to prevent movement of the sample. All vials were heat sealed to prevent loss of sample, and all test portions were weighed to the nearest 0.1 mg.

Standards were prepared by pipetting stock solutions onto Whatman filter paper cut to fit the inside of a small vial (2.8 cm x 1.9 cm). The filter papers were dried under a heat lamp before being placed in the vials. The stock solutions were prepared by dilution of 1000 µg/ mL atomic absorption standards (Fisher Scientific Co.). The small vials were heat sealed and packed as for the biological materials.

Standard reference materials used were NIST 1577a Bovine Liver, 1575 Pine Needles, 1572 Citrus Leaves, and 1567 Wheat Flour; NRC TORT-1, DOLT-1, and DORM-1; and NIES Pepperbush.

4.4.2 Irradiation and Counting

The irradiation and counting operations were carried out at the SLOWPOKE II reactor facility of the University of Alberta. The irradiation-decay-count scheme used was 210 s irradiation, 10 s decay, and 210 s count. All samples discussed in this chapter were irradiated in site 5 of the reactor at a flux of 1×10^{12} n $cm^{-2}s^{-1}$ and were counted at a sample to detector distance of 10 cm.

Counting was carried out on an ORTEC 86 cm^3 active volume WIN-15 coaxial Ge(Li) detector with an ORTEC 472A amplifier and a Nuclear Data (ND) 575 ADC. Detector specifications include an efficiency of 18.5% relative to a NaI detector, a measured FWHM of 2.1 keV and a peak-to-compton ratio of 53:1 for the 1332 keV photopeak of ^{60}Co.

The specific activities (counts/microgram for each radionuclide) were determined for each counting period, and the masses of the elements in the standards were determined via an adaptation of the comparator (semi-absolute) method for INAA (110), that is, by dividing the photopeak areas of the unknowns by the specific activities of the relevant radionuclides. Deadtime corrections (111) for the decay of short-lived radioisotopes in the presence of active, long-lived isotopes such as ^{24}Na and ^{38}Cl were applied to each peak. In addition, a correction factor for random summing effects was calculated and applied following the procedure of Wyttenbach (112). All calculations and statistics were done on an Apple Macintosh computer using the Excel or Statworks packages and are given in Appendix 2.

4.5 RESULTS AND DISCUSSION

The results of the Al analyses are shown in Tables 4.1 and 4.2. All uncertainties are one standard deviation. Two or three subsamples were taken from each bottle. Bran 186 has the lowest Al concentration and at this level the scatter is large. Whole Milk Powder also has a large amount of scatter. According to the AA results Whole Milk Powder has very low Al values and this scatter may be due to variability in the phosphorus and silicon content of this material.

Results for the reference materials are shown in Table 4.3. These results have not been corrected for phosphorus or silicon and should not be compared with the certified values.

All data were tested for outliers at the 90% confidence level using the Dean and Dixon Q test (97). A one way analysis of variance was performed on the agricultural materials to determine the between vs. within bottle homogeneity. The table value for 3 between and 6 within bottle degrees of freedom is 4.76 (98). The F ratios for the samples are given in Table 4.4. The calculated Bran F ratio is higher than the table value but this is not unusual considering the large amount of scatter in the results.

The F ratio for Meat is also higher than the table value. This is due to the differences in averages obtained for the bottles. Bottle 1817 has an average value of 15.32 and bottle 3019 has an average value of 11.78. The F ratio indicates there is a significant difference between bottles. This difference might be eliminated by analyzing more samples per bottle.

Also shown in Table 4.4 are the contributions of the measurement and sampling uncertainties to the overall uncertainty. For this calculation the average measurement standard deviation was used. For Bran no s_s can be calculated because the average measurement standard deviation is larger than the overall standard deviation. This is not surprising since the aluminum concentration of Bran falls at the detection limit of the method. Gluten and Starch have measurement and sampling uncertainties of about 50% of

the overall uncertainty. These materials have aluminum values above the detection limit and reproducibility seems to be good. The reason for the high measurement uncertainty for these materials is unknown. A non-uniform particle size may be the result but this did not seem to affect the AA aluminum values.

Table 4.1 INAA Results for Al in Agricultural Materials*.

Bottle No.	FLOUR 187	Bottle No.	GLUTEN 184	Bottle No.	BRAN 186
488	19.03 ± 0.48	532	13.13 ± 0.56	312	0.753 ± 0.259
	18.32 ± 0.49		13.53 ± 0.55		0.838 ± 0.261
	20.28 ± 0.50				0.703 ± 0.261
Average	19.21 ± 0.99	Average	13.33 ± 0.28	Average	0.765 ± 0.068
640	20.38 ± 0.50	639	13.87 ± 0.58	390	1.268 ± 0.282
	18.13 ± 0.48		14.87 ± 0.58		0.921 ± 0.272
			17.76 ± 0.62		
Average	19.26 ± 1.59	Average	15.50 ± 2.02	Average	1.090 ± 0.240
935	17.30 ± 0.48	1288	14.15 ± 0.55	927	0.398 ± 0.241
	18.29 ± 0.48		15.41 ± 0.60		0.566 ± 0.250
Average	17.84 ± 0.64	Average	14.78 ± 0.89	Average	0.482 ± 0.119
971	17.94 ± 0.49	1328	13.55 ± 0.57	1428	0.520 ± 0.248
	18.75 ± 0.49		12.99 ± 0.52		0.828 ± 0.263
Average	18.34 ± 0.57	Average	13.27 ± 0.40	Average	0.674 ± 0.220
Overall Ave	18.72 ± 1.02		13.94 ± 0.84		0.755 ± 0.256

CORN KERNEL	CORN STALK
7.29 ± 0.45	87.4 ± 0.5
7.02 ± 0.39	138 ± 0.6
7.83 ± 0.48	93.7 ± 0.5
	96.5 ± 0.6
	117 ± 0.6
Overall Ave. 7.38 ± 0.41	106 ± 21

* Without correction for interference by phosphorus and silicon.

Table 4.2 INAA Results for Al in Agricultural Materials*.

Bottle No.	WHOLE EGG POWDER 183	Bottle No.	WHOLE MILK POWDER 188	Bottle No.	MEAT 136
329	588 ± 1	295	12.15 ± 0.46	57	13.25 ± 0.73
	625 ± 1		15.50 ± 0.43		14.50 ± 0.77
Average	606 ± 26	Average	13.82 ± 2.37	Average	13.88 ± 0.88
512	587 ± 1	997	5.16 ± 1.38	422	14.05 ± 0.72
	600 ± 1				15.83 ± 0.76
	598 ± 1				
Average	595 ± 7	Average	5.16 ± 1.38	Average	14.94 ± 1.26
751	584 ± 1	1234	9.85 ± 0.59	1817	15.32 ± 0.81
	602 ± 1		11.22 ± 1.84		15.01 ± 0.78
			3.81 ± 1.34		15.62 ± 0.79
Average	593 ± 13	Average	8.29 ± 3.94	Average	15.32 ± 3.05
1930	599 ± 1	1262	8.95 ± 1.58	3019	11.52 ± 0.64
	594 ± 1		13.62 ± 2.44		12.05 ± 0.71
Average	596 ± 4	Average	11.28 ± 3.30	Average	11.78 ± 3.75
Overall Ave.	597 ± 12		10.03 ± 4.00		14.13 ± 1.55

Bottle No.	CELLULOSE 189	Bottle No.	STARCH 162
479	5.39 ± 0.36	140	1.84 ± 0.31
	4.10 ± 0.34		1.83 ± 0.30
	3.60 ± 0.33		1.82 ± 0.32
Average	4.36 ± 0.92	Average	1.83 ± 0.01
497	3.47 ± 0.33	412	2.93 ± 0.34
	4.27 ± 0.35		1.83 ± 0.31
Average	3.87 ± 0.56	Average	2.38 ± 0.78
662	4.29 ± 0.34	869	2.08 ± 0.32
	3.62 ± 0.33		1.26 ± 0.29
Average	3.95 ± 0.47	Average	1.67 ± 0.58
1791	3.97 ± 0.34	1591	2.59 ± 0.35
	6.93 ± 0.40		1.82 ± 0.30
Average	5.45 ± 2.09	Average	2.20 ± 0.54
Overall Ave.	4.40 ± 1.11		2.00 ± 0.49

* Without correction for interference by phosphorus and silicon.

Table 4.3 Al in Standard Reference Materials by INAA*.

	BOVINE LIVER	WHEAT FLOUR	CITRUS LEAVES
	19.84 ± 1.03	6.83 ± 0.41	91.04 ± 0.70
	17.07 ± 0.94	6.70 ± 0.43	91.24 ± 0.71
		8.44 ± 0.46	
Overall Ave.	18.46 ± 1.96	7.32 ± 0.97	91.14 ± 0.14
Cert. Value	(2)	(17)	92 ± 15
	DOLT-1	DORM-1	PINE NEEDLES
	24.81 ± 1.72	31.27 ± 1.98	583 ± 1
	18.33 ± 1.30	31.95 ± 1.32	601 ± 1
Overall Ave.	21.57 ± 4.58	31.44 ± 0.72	592 ± 13
Cert. Value	(7)	(21)	545 ± 30
	TORT-1	PEPPERBUSH	
	92.65 ± 1.43	664 ± 1	
	52.31 ± 0.89	586 ± 1	
Overall Ave.	74.48 ± 28.5	625 ± 55	
Cert. Value	(42 ± 2)	(513 ± 138)	

* Without correction for interference by phosphorus and silicon.

Table 4.4 Standard Deviation in μg Al/g due to Sampling.

Sample	Calculated F Ratio	s_o[a]	s_m[a]	s_s[a]	Fraction of s_o due to s_s
Flour	0.99	1.02	0.49	0.89	0.76
Gluten	1.59	1.50	0.57	0.62	0.41
Bran	5.00	0.26	0.26	*	*
Egg Powder	0.39	12	1	12	1.00
Milk Powder	0.81	4.00	1.26	3.55	0.89
Meat	10.4	1.55	0.74	1.36	0.77
Cellulose	0.80	1.11	0.35	1.05	0.89
Starch	0.91	0.49	0.32	0.37	0.57

* No s_s calculated because of large s_m.

[a] s_o, s_m and s_s are the overall, measurement and subsampling standard deviations.

CHAPTER 5

DETERMINATION OF PHOSPHORUS BY DERIVATIVE ACTIVATION ANALYSIS FOR CORRECTION OF ALUMINUM INTERFERENCES

5.1 INTRODUCTION

Phosphorus in biological materials can be determined in a variety of ways. Probably the oldest method is spectrophotometric measurement of the blue phosphomolybdate complex. The yellow phosphovanadomolybdate complex has also been used. In both cases careful control of pH, ionic strength, time from mixing to measurement, and reducing agent concentration is necessary for satisfactory results. Formation of these complexes can be used to determine phosphorus in clinical samples (113,114) and in water and wastewater (115).

Lin et al. (116) used an Auto Analyzer and Maher et al. (117) used flow injection to determine phosphorus from phosphovanadomolybdate complexes. Narusawa et al. (118) simultaneously determined silicon and phosphorus by forming the molybdate complexes. Bowman (119) also used the molybdate complex to determine both in plant material.

Atomic absorption spectrometry (AAS) is becoming more widely used to determine phosphorus but since the resonance lines of phosphorus lie in the vacuum ultraviolet (178.287 and 177.499 nm) most present instrumentation is not equipped for this determination. The non-resonance line at 213.618 nm can be used but poor sensitivity results.

Pramod and Ramchandran (120) complexed phosphorus to bismuth and molybdenum and indirectly determined phosphorus by determining bismuth by AAS. Lin et al. (113) and Casetta et al. (121) used zirconium coated graphite tubes. When compared with colorimetric methods accuracy and reproducibility were only slightly improved. Ohta et al. (122) used a molybdenum tube atomizer for the electrothermal atomic absorption spectrometric (ETAAS) determination of phosphorus. They found that sensitivity, accuracy, and precision were better than or equal to graphite furnace atomic absorption spectrometry (GFAAS).

Phosphorus can be determined by neutron activation analysis (NAA) but requires two irradiations. Phosphorus forms ^{28}Al via an (n, α) reaction and the phosphorus contribution to Al must be determined by irradiating with thermal and then epithermal neutrons and calculating the difference. Gatschke (123) and Lavi et al. (124) determined phosphorus and aluminum in biological materials in this way.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is by far the most popular method for determining phosphorus in biological materials. Conventional wet and dry ashing (46,125), fusion with Li_2CO_3/H_3BO_3 (118) and microwave digestion (51,125) have been used for sample dissolution. Kumpulainen et al. (126), Jones (127), White (128) and Bowman (119) have also used ICP-AES to determine phosphorus and have compared the results with other methods. However, an ICP equipped to measure phosphorus was not available for this work.

Derivative activation analysis (DAA) was chosen as the method for phosphorus determination since it can be used to increase the sensitivity of neutron activation analysis and does not require a double irradiation using thermal and epithermal neutron bombardment. A procedure using complexation of phosphorus with vanadium and molybdenum to form the phosphovanadomolybdate complex was employed which allows indirect determination of phosphorus by irradiation and counting of ^{52}V. This method has all the limitations of the photometric method where P is determined as the phosphovanadomolybdate but in this case the sensitivity is better and the loss of color intensity with time is not important. The background for this indirect method is discussed in the following paragraphs.

The element of interest, M, is complexed with or exchanged for an element for which neutron activation has a high sensitivity. This is called the indicator element. The indicator element, I, should have one or more of the following properties (128):(a) a relatively large thermal neutron cross section, (b) a short half life for the nuclide produced (but long enough to be counted accurately), (c) one or more gamma rays of high

abundance (with minimal spectral interferences) resulting from the decay of the radionuclides produced, and (d) a high isotopic abundance for the target nuclide.

Several characteristics are desirable for the indicator system (129): (a) the indicator element should be associated with the element of interest in a stoichiometric ratio of 1:1 or greater, (b) the excess quantity of indicator element remaining after complexation should be easily removed, and (c) the final complex should be relatively stable.

Three methods are available by which the element of interest M is replaced by the indicator element, I (129):

1. M and I are complexed and then separated from excess I, usually by extraction of the complex into an organic solvent. The activity of the organic phase is used as an indirect measurement of M .

2. M is exchanged for I which was previously complexed in an organic phase. The released I is used to measure the amount of M originally present.

3. I is complexed and isolated by extraction into an organic solvent. I is exchanged for M to form a complex in the organic phase.

DAA has several advantages over conventional radiochemical techniques. The major ones are that elements which cannot usually be determined by NAA may be determined with high sensitivity and no handling of radioactive solutions is involved. The principal disadvantages are that (a) the method is destructive (unlike nondestructive NAA), that is, the sample must be dissolved, (b) the solution processing may lead to loss of the element of interest, and (c) the procedures must be quantitative or of known yield.

There are few references in the literature to DAA. Smathers et al. (130) used 5,7-dibromo-8-hydroxyquinoline to chelate magnesium. The ^{82}Br activity produced on irradiation of the complex was used as an indirect measurement of magnesium. The complex and excess complexing agent were separated by two dimensional paper chromatography. Cheng et al. (131) used parabromobenzoyl trifluoroacetone to chelate Fe^{+2} and Fe^{+3}, which allowed species differentiation (speciation), an advantage not

available to conventional NAA. Again paper chromatography was used for separation. Allen and Hahn (132) determined phosphorus by formation of a tungstomolybdate phosphate complex. Measurement of the ^{187}W activity gave an indirect measure of the phosphorus.

Several biological compounds have been determined by tagging with derivatives containing bromine (133). Separations were effected by paper chromatography and the papers were irradiated. Stein and Benson also formed fatty acid-mercury complexes that were irradiated to produce ^{203}Hg. Young (129) has used DAA to determine phosphorus and thallium in a variety of matrices. Phosphovanadomolybdate and thallium iodonitrotetrazolium chloride complexes were used. The complexes were extracted into organic solvents, irradiated, and the vanadium and thallium activities measured.

Kleppinger et al. (134) and Oltmann and Ryan (135) have also used phosphovanadomolybdate complexes to determine phosphorus by extraction into an organic solvent, followed by irradiation. The complex formed is $H_4(PMo_{11}VO_{40})$. This form is stable in acidic medium ($[H^+]<0.8M$) (136,137). Although other forms of this complex can be used at different pH values, this form is the most stable and the most analytically useful (138). At low pH all forms of this heteropoly acid degrade to the most stable form as follows:

$$11(PV_6Mo_6O_{38})^{5-} + 115H^+ \rightarrow 6(PVMo_{11}O_{40})H_4 + 60VO_2^+ + 5H_3PO_4$$

$$11(PV_{10}Mo_2O_{37})^{7-} + 185H^+ \rightarrow 2(PVMo_{11}O_{40})H_4 + 108VO_2^+ + 9H_3PO_4$$

To ensure that only one form is present the pH should be less than 1.

5.2 EXPERIMENTAL

5.2.1 Sample Preparation

Four bottles each of Bran, Flour, Gluten, Whole Egg Powder, Wholw Milk Powder, Meat, Starch and Cellulose were obtained from Agriculture Canada, Ottawa. One bottle each of Corn Kernel and Corn Stalk were purchased from the National Institute for Science and Technology. All samples were tumbled end-over-end for at least 2 hours.

After tumbling, about 5-g portions were transferred to clean, dry glass weighing bottles and dried at 85°C for 4 hours.

5.2.2 Sample Digestion

Approximately 50 mg of Whole Milk Powder, Whole Egg Powder and Meat; 125 mg of Flour, Gluten and Corn Kernel; and 250 mg of Bran, Starch, Cellulose and Corn Stalk were weighed into 50-mL Teflon beakers and 5 mL of concentrated HNO_3 added. The beakers were placed inside a 4-litre plastic pail with a tight fitting lid and placed on the turntable inside a 700-watt microwave oven (Sears Kenmore). The samples were heated for 3 minutes at 15% power. After 3 minutes the pail was vented to remove the build up of nitrogen oxides. The samples were heated for another 1 and 1/2 minutes and then placed on a sandbath for about 1 hour at 100°C. After cooling, 1 mL of $HClO_4$ was added and the samples were heated on a sandbath at 200° in a perchloric acid hood until fuming (CAUTION: Perchloric acid should only be evaporated in hoods designed for this purpose to avoid explosions.). After cooling, Whole Egg Powder, Whole Milk Powder, Meat, Flour, Gluten and Corn Kernel were diluted to 100 mL in volumetric flasks. Bran, Starch, Cellulose and Corn Stalk were diluted to 25 mL.

5.2.3 Extraction Procedure

A 25-mL portion of sample was placed in a 125-mL separatory funnel. Five mL of concentrated HNO_3 , 5 mL of 0.01 M ammonium vanadate (NH_4VO_3) and 10 mL of 0.1 M ammonium molybdate [$(NH_4)_6Mo_7O_{24}4H_2O$] were added with swirling between each addition. The pH was checked to ensure that it was not greater than 1.0. The solution was allowed to stand for 30 minutes to allow formation of the phosphovanadomolybdate complex. After 30 minutes 5 mL of methyl isobutyl ketone (MIBK) was added and the mixture was shaken for 5 minutes at 30 second intervals. The layers were then allowed to separate for 1

hour. After separation the MIBK layer was collected in 10-mL Teflon tubes and frozen until irradiation.

5.2.4 Sample Packing

Vials were precleaned by ultrasonication in Contrad 70 for 45 minutes. After rinsing with distilled water the vials were sonicated in 95% ethanol for 45 minutes and allowed to air dry. For irradiation 1 mL of the MIBK layer was pipetted into a precleaned 1.5-mL polyethylene vial. The vial was immediately heat sealed to prevent loss of the organic solvent. These small vials were placed in larger irradiation vials (7 mL) and another small vial containing cotton wool was placed on top to serve as a spacer and to act as an absorbent in case of leaks. The large vial was also heat sealed.

5.2.5 Standards

Standard solutions are prepared from a 1000 μg P/mL stock solution of KH_2PO_4 (Aldrich). The stock solution was prepared by dissolving 0.4394 g of KH_2PO_4 in 100 mL of distilled deionized water. The standards were extracted and packed as described for the samples.

Certified reference materials used were NIST 1566 Oyster Tissue, 1573 Tomato Leaves, 1572 Citrus Leaves, 1575 Pine Needles, and 1567 Wheat Flour, and NRC TORT-1.

5.2.6 Irradiation and Counting

The irradiation and counting operations were carried out at the SLOWPOKE II reactor facility of the University of Alberta. The irradiation-decay-count scheme used was 240 s irradiation, 60 s decay, and 240 s count. The irradiations were done in site 1 of the reactor at a flux of 1×10^{11} n $cm^{-2}s^{-1}$ or 1×10^{12} n $cm^{-2}s^{-1}$ and were counted at a sample to detector distance of 3 cm. Counting of the 1434 keV line was carried out on a GEM 20180 hyperpure Ge detector coupled to a ND 660 multichannel analyzer with an ORTEC 572

amplifier and ND 575 ADC. Detector specifications include an efficiency of 22.4% relative to a NaI detector, a measured FWHM of 1.7 keV and a peak-to-compton ratio of 59:1.

The specific activities (counts/microgram for each radionuclide) were determined for each counting period, and the masses of the elements in the NIST and NRC standards were determined via an adaptation of the comparator (semi-absolute) method for INAA (110), that is, by dividing the photopeak areas of the unknowns by the specific activities of the relevant radionuclides. Deadtime corrections (111) for the decay of short-lived radioisotopes in the presence of active, long-lived isotopes such as ^{24}Na and ^{38}Cl were applied to each peak. In addition, a correction factor for random summing effects was calculated and applied following the procedure of Wyttenbach (112). All calculations and statistics were done on an Apple Macintosh computer using the Excel or Statworks packages and are given in Appendix 3.

5.3 RESULTS AND DISCUSSION OF PHOSPHORUS DETERMINATION

For the initial digestions of these samples a combination of HNO_3 and H_2SO_4 followed by $HClO_4$ was used. This method tended to give low results for the reference materials. It was thought that H_2SO_4 was causing formation of polyphosphates by dehydration. Since PO_4^{3-} is the major form of P present and is not volatile, the phosphate may be converted to a form not available to complex V and Mo. As a result H_2SO_4 was omitted from further digestions. A second digestion procedure was then tried; this one consisted of HNO_3 followed by H_2O_2. This method gave scattered results and the final solution was often cloudy and yellow. A third method using HNO_3 followed by $HClO_4$ was tried next. This sequence gave the most consistent results and was used throughout. A comparison of results using the three methods is provided in Table 5.1.

Results of the phosphorus determinations on the various agricultural materials using the third method are given in Tables 5.2 and 5.3. Bran and Starch have fewer values than

the other materials because the phosphorus levels in these two materials are near the detection limit of the method and reproducible values are difficult to obtain. A number of subsamples of Bran and Starch gave results below the detection limit and are not included in the table. Cellulose is a polysaccharide made up of glucose units. Because of this structure cellulose would not be expected to contain phosphorus, and none was detected in this study.

Results for the analyses of phosphorus in the reference materials are given in Table 5.4. All data in Tables 5.2 to 5.4 were tested for outliers using the Dean and Dixon Q test (97). Only two results out of 102 were rejected. These values are marked in the tables with an asterisk. A one way analysis of variance was run on the data to test for statistical differences in within vs. between bottle homogeneity. The table F ratio for 3 between bottle and 11 within degrees of freedom is 3.59 at the 95% confidence level (98). The experimentally determined F ratios for all materials are given in Table 5.5 . All F ratios are below the table value. This indicates that phosphorus is homogeneous in these materials at the sample size and confidence level used.

To determine the uncertainty due to the subsampling, analytical procedure (extraction) and counting steps the following procedure was used. Two subsamples from each bottle were taken. Each subsample was dissolved and diluted to volume. From one subsample one portion (25mL) was taken for extraction. For 2 of the 4 bottles 2 portions of the second subsample were taken for extraction. This replication was done to determine the extraction uncertainty. Each of these 2 portions of the second subsample were extracted and 1 mL of the organic phase was sealed in an irradiation vial. This organic phase was irradiated twice and counted twice to determine the counting uncertainty. For each material the average counting uncertainty and the average procedural uncertainty were used to determine the subsampling uncertainty. These values along with the overall uncertainty are given in Table 5.5. These calculations were done for all the materials except Starch, Bran, Corn Kernel and Corn Stalk. The results show that in most materials the subsampling

uncertainty contributes the largest fraction to the overall uncertainty. For Meat the extraction procedure was the largest fraction of the overall uncertainty. The reason for this is unknown. The next lowest contribution of subsampling to the overall uncertainty is for Gluten (57%). This trend follows the same pattern as the aluminum by INAA values. Particle size may again be the cause. The other three materials have subsampling as the major source of uncertainty, as expected.

5.4 CONCLUSIONS

From the results presented it can be concluded that the dissolution, extraction, and measurement procedure for phosphorus used here gives reasonably reliable results for this element in a variety of agricultural materials. The procedure has a detection limit of about 1.0 μg per gram for most materials, and a relative standard deviation on the order of 10%. Comparison of the analytical results obtained here with reported values for the reference materials studied shows our results to trend to the low side, but to be generally within the 95% tolerance levels for these materials. The largest source of uncertainty in the results was shown in all but one case to be the subsampling step.

The derivative activation analysis method works well for the determination of phosphorus in most materials. The precision of the method is good but greatly decreases near the detection limit to about 50%, as in the case for Bran. When correcting aluminum results for phosphorus interference this method works well, unless the aluminum level is low and the phosphorus is high. This is discussed in more detail in the following section.

5.5 CORRECTION OF ALUMINUM RESULTS FOR INTERFERENCE BY PHOSPHORUS

Table 5.6 shows the aluminum values determined by INAA before and after correction for phosphorus. Whole Milk Powder gives a corrected value of less than zero. Since the AA result for Whole Milk Powder was near the detection limit it is clear that the aluminum

signal given by INAA was affected by the presence of phosphorus and that aluminum was below the detection limit of INAA. In general the DAA method of phosphorus analysis works well except in cases where the aluminum is low and the phosphorus is high. The correction fails if the ratio of phosphorus to aluminum concentration is greater than about 5000 (this is the P:Al ratio for Bovine Liver). At this level the standard deviation is as large as the value. At P:Al ratios above this level the aluminum signal is due almost totally to phosphorus, and even though a corrected aluminum value might be obtained, the standard deviation would be excessively large. The P:Al ratio for Whole Milk Powder using the AA aluminum value is over 16,000, and so the procedure is unuseable.

In general, where applicable the corrected aluminum values agree well with the AA values, considering that a correction for silicon has yet to be done. Table 5.6 gives the GFAAS results from Chapter 2 to allow more convenient comparison.

Table 5.1. Determination of Phosphorus in Standard Reference Materials Using Different Digestion Techniques.

Sample	HNO_3+H_2SO_4 then $HClO_4$	HNO_3 then H_2O_2	HNO_3 then $HClO_4$	Cert. Value, µg/g
TORT-1	7907	9167	8264	8790 ± 210
Bovine Liver	8807	N.D.	11148	11100 ± 400
Oyster Tissue	7070	7741	7149	8100
Tom. Leaves	3184	3953	3273	3400 ± 200
Citrus Leaves	1181	1207	1229	(1300 ± 200)
Pine Needles	1088	1095	1091	1200 ± 200
Wheat Flour	1225	N.D.	N.D.	(1390 ± 30)

N.D. Not Determined

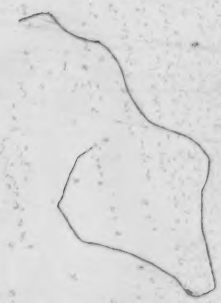

Table 5.2 INAA Results for Phosphorus in Agricultural Materials in μg/g.

Bottle No.	FLOUR 187	Bottle No.	GLUTEN 184	Bottle No.	BRAN 186
488	2110 ± 8	532	1630 ± 6	312	117 ± 0.7
	2311 ± 9		1615 ± 6		
	2302 ± 9		1737 ± 7		
	2282 ± 9		1528 ± 8		
	2314 ± 14		1566 ± 6		
Average	2302 ± 14	Average	1615 ± 79		**
640	2497 ± 10	639	1544 ± 5	390	59 ± 0.5
	2323 ± 9		1571 ± 6		125 ± 0.7
			1485 ± 7		112 ± 0.7
			1518 ± 6		
			1469 ± 4		
Average	2410 ± 123	Average	1517 ± 42		**
935	2148 ± 6	1288	1726 ± 5	927	56 ± 0.5
	2243 ± 13		1543 ± 6		136 ± 0.7
	2190 ± 9				
	2284 ± 9				
	2208 ± 9				
Average	2215 ± 52	Average	1634 ± 129		**
971	2332 ± 9	1328	1591 ± 8	1428	45 ± 0.4
	1986 ± 8		1447 ± 13		131 ± 0.8
Average	2159 ± 245	Average	1519 ± 102		**
Overall Ave.	2222 ± 121		1569 ± 86		94 ± 38

Bottle No.	CELLULOSE	Bottle No.	STARCH
479	<1.0	140	163 ± 0.6
			178 ± 0.7
497	<1.0	412	***
662	<1.0	869	169 ± 0.7
			181 ± 0.5
1797	<1.0	1591	164 ± 0.6
			165 ± 0.5
Overall Ave.	<1.0		170 ± 8.0

** Because of scatter, calculation of average was not considered appropriate for individual bottles.

*** No values obtained on samples from this bottle.

Table 5.3 INAA Results for Phosphorus in Agricultural Materials in μg/g.

Bottle No.	WHOLE EGG POWDER	Bottle No.	WHOLE MILK POWDER	Bottle No.	MEAT
329	8119 ± 40	295	6831 ± 20	57	8194 ± 24
	8789 ± 26		6861 ± 20		7638 ± 23
			7101 ± 21		
			7034 ± 21		
			7064 ± 31		
			7202 ± 20		
Average	8454 ± 474	Average	7016 ± 143	Average	7916 ± 393
512	9585 ± 29	997	7303 ± 22	422	8128 ± 24
	8221 ± 25		7167 ± 22		7642 ± 23
	7950 ± 24		7094 ± 21		7673 ± 23
	7803 ± 23		7083 ± 21		7929 ± 40
	7753 ± 23		7066 ± 21		7709 ± 31
Average	8262 ± 761	Average	7143 ± 98	Average	7816 ± 208
751	8675 ± 35	1234	7538 ± 23	1817	7963 ± 24 *
	8485 ± 25		6898 ± 21		7484 ± 22
					7545 ± 23
					7713 ± 23
					7606 ± 23
Average	8580 ± 134	Average	7218 ± 452	Average	7594 ± 101
1930	8033 ± 24	1262	7428 ± 22	3019	7874 ± 24
	8020 ± 24		6896 ± 21		7494 ± 22
	7950 ± 24				
	8112 ± 24				
	8031 ± 24				
Average	8029 ± 58	Average	7162 ± 376	Average	7684 ± 296
Overall Ave.	8252 ± 490		7104 ± 202		7741 ± 227

	CORN KERNEL	CORN STALK
	1630 ± 5	528 ± 2
	1778 ± 4	549 ± 2
	1720 ± 3	508 ± 2
	1715 ± 5	572 ± 2
	1442 ± 4 *	538 ± 2
	1735 ± 5	541 ± 2
		509 ± 2
Overall Ave.	1716 ± 54	535 ± 22

* Rejected by Q test.

Table 5.4 INAA Results for Phosphorus in Standard Reference Materials in μg/g.

	TORT-1	OYSTER TISSUE	BOVINE LIVER
	8264 ± 24	7149 ± 36	11148 ± 33
	7972 ± 24	6665 ± 20	10660 ± 32
	8134 ± 24	6988 ± 21	
Overall Ave	8118 ± 206	6934 ± 246	10904 ± 345
Cert. Value	8790 ± 10	8100	11100 ± 400
	CITRUS LEAVES	TOMATO LEAVES	PINE NEEDLES
	1229 ± 7	3273 ± 10	1091 ± 5
	1024 ± 4	2954 ± 9	937 ± 4
	1146 ± 5	3160 ± 9	1014 ± 4
Overall Ave	1133 ± 103	3129 ± 162	1014 ± 77
Cert.Value	(1300 ± 200)	3400 ± 200	1200 ± 200
	WHEAT FLOUR		
	1047 ± 4		
	1118 ± 5		
	1156 ± 5		
Overall Ave	1107 ± 45		
Cert. Value	(1390 ± 30)		

Table 5.5 Standard Deviation in µg P/g due to Sampling.

Sample	Calculated F Ratio	s_o[a]	s_{count}	s_{ext}	s_s	Fraction of s_o due to s_s
Flour	2.16	109	30	14	104	0.91
Gluten	2.12	102	33	58	77	0.57
Bran	0.08	41	NC	NC	NC	NC
Egg Powder	0.71	490	83	140	462	0.89
Milk Powder	0.66	376	70	51	365	0.94
Meat	0.76	142	69	114	49	0.12
Starch	0.90	7	NC	NC	NC	NC

NC Not calculated.

[a] s_o, s_{count}, s_{ext} and s_s are the overall, counting extraction and subsampling standard deviations.

Table 5.6 INAA Results for Aluminum after Correction for Phosphorus

Sample	Meas. Al, µg/g	P, µg/g	Correction Factor	Corrected Al, µg/g	Al by AA, µg/g	Certified or Literature Value	P:Al Ratio
Flour	19 ± 1	2272 ± 109	3.4 ± 0.2	15 ± 1	13± 1	NA	148
Gluten	14 ± 1	1569 ± 86	2.4 ± 0.1	12 ± 1	11 ± 1	NA	135
Bran	0.8 ± 0.3	94 ± 41	0.14 ± 0.06	0.6 ± 0.3	1.4 ± 0.3	NA	154
Egg Powder	597 ± 12	8252 ± 490	12.4 ± 0.7	585 ± 12	499 ± 39	NA	14
Meat	14.1 ± 0.5	7752 ± 142	11.6 ± 0.2	2.5 ± 0.6	1.0 ± 0.3	NA	3076
Milk Powder	10 ± 4	7104 ± 202	10.6 ± 0.3	–	0.4 ± 0.2	NA	16109
Cellulose	4.4 ± 1.1	< 1.0	a	4.4 ± 1.1	3.8 ± 0.7	NA	0.02
Starch	2.0 ± 0.2	170 ± 8	0.25 ± 0.01	1.8 ± 0.2	2.2 ± 0.6	NA	97
Corn Kernel	7.4 ± 0.4	1716 ± 54	2.6 ± 0.1	4.8 ± 0.4	3.9 ± 0.3	4 ± 2[b]	357
Corn Stalk	106 ± 21	535 ± 22	0.80 ± 0.03	105 ± 21	76 ± 5	118 ± 14[b]	5
Bovine Liver	18 ± 2	10904 ± 345	16.3 ± 0.5	2.1 ± 2	1.7 ± 0.5	(2)	5119
Wheat Flour	7 ± 1	1107 ± 45	1.7 ± 0.1	6 ± 1	ND	(17)	195
Citrus Leaves	91.1 ± 0.1	1133 ± 103	1.7 ± 0.2	89.4 ± 0.2	ND	92 ± 15	13
Pine Needles	592 ± 13	1014 ± 77	1.5 ± 0.1	590 ± 13	520 ± 13	545 ± 30	1.7
TORT-1	74 ± 28	8118 ± 206	12.2 ± 0.3	62 ± 28	42 ± 4	42 ± 2	131
Pepperbush	625 ± 55	1100	1.65	623 ± 55	ND	(513 ± 138)	1.8

NA Not available.

ND Not determined.

[a] No correction due to low phosphorus.

[b] Literature value.

CHAPTER 6

PRELIMINARY STUDIES ON THE DETERMINATION OF SILICON BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

6.1 INTRODUCTION

Silicon is generally a very difficult element to determine because of its refractory nature and because it is difficult to dissolve. Silicon can be determined gravimetrically as SiO_2 (139). Titrimetric methods are usually based on the properties of silicomolybdic and fluosilicic acids since silicic acid cannot be directly determined by titration (139).

Photometric methods for the determination of silicon are widely used. Most often silicon is determined as the yellow silicomolybdate complex at 352 nm (139). The rate of formation of the silicomolybdate complex depends on the degree of polymerization of silicic acid (139). Addition of reducing agents to the yellow heteropoly acid produces an intense blue color . This method is about 5 times more sensitive than determination of the yellow heteropoly acids (139). Reay and Bennett determined amorphous and total silicon in plant materials using the molybdenum blue method (140). Morrison and Wilson determined silicon in water using this method (141).

Several methods for silicon determination involve separation of silicon by distillation as SiF_4 . The SiF_4 is collected in an absorbing solution and then determined photometrically as the molybdenum blue complex (142-144) or gravimetrically as the quinoline molybdosilicate (145).

Silicon has also been determined by graphite furnace atomic absorption spectroscopy (GFAAS) but there are few practical methods (41). Lo and Christian studied the reaction of silicon in the graphite furnace and determined that silicon carbide was formed (146). This formation led to an increased signal with increasing temperature. The addition of lanthanum, which also forms a carbide, reduced the problem of silicon carbide

formation; however, lanthanum silicides may be formed. HCl, HNO_3 and oxide containing substances suppress absorbance while chloride salts enhance absorbance (146). Despite these problems Lo and Christian reported satisfactory analytical results for silicon in blood, serum and urine (147). Bloc and Walter measured silicon in honeydew melon (148). Berndt and Schaldach used a tungsten coil atomizer in electrothermal atomization absorption spectroscopy but found GFAAS to be better (149).

Nater and Burau published a method for trace silicon analysis using alkali metal fluorides and HF as matrix modifiers (150). Graphite tubes were pretreated by soaking them in a zirconium solution to decrease silicon carbide formation. This method was used only on aqueous standards.

Inductively coupled plasma atomic emission spectrometry is another method that has been used for silicon determination. Matrices included food samples (151) and biological materials (152,153).

X-ray fluorescence is a popular method for silicon analysis. Gladney et al. determined silicon in a series of biological materials by X-ray fluorescence and epithermal neutron activation analysis (ENAA) (154). Crecelius (155) and Williamson et al. (156) also used ENAA for silicon determination. Zeisler et al. (157) and Gorbunov et al. (158) determined several elements by combined X-ray fluorescence and neutron activation; in both cases silicon was determined by X-ray fluorescence alone.

In this study we decided to concentrate on GFAAS as the analytical method for silicon. This decision was based primarily on previous success with a similar procedure for silicon in biological materials in our hands. We also did some exploratory work on the use of ICP-MS for silicon.

6.2 EXPERIMENTAL

6.2.1 Apparatus

Atomic absorption measurements of silicon were made on a microprocessor controlled spectrophotometer (Perkin Elmer Model 5000). A deuterium lamp was used for background correction. An HGA 2200 furnace with 3 stage programming was used for atomization of the sample and an AS-1 autosampler with fixed 20 µL injection was used to inject samples into the furnace. Pyrolytically coated graphite tubes with solid pyrolytic graphite platforms were used (Perkin Elmer part numbers 0290-1822 and B012-1091). The tubes and platforms were pretreated by putting them in a flask containing 50 mL of a 1000 µg/mL solution of $Zr(NO_3)_4$ (150) and drawing a vacuum. Upon return to normal atmospheric pressure the zirconium solution flowed into the pores of the graphite. Air bubbles had to be shaken from the tubes and platforms prior to release of the vacuum. The vacuum cycle was continued until no bubbles formed on the graphite surface. The tubes were then dried in an oven at 70°C for 24 hours. Before use the ends of the tubes were polished with a Kimwipe to increase electrical conductivity between the graphite tube and graphite cones in the furnace assembly. Operating conditions were as follows: wavelength 251.6 nm; integration time 3 sec; slit width 0.2 nm; drying temperature and time 160°C, 70 sec; ashing temperature and time 1150°C, 45 sec; atomization temperature and time 2500°C, 3 sec; HCL current, 16 mA. The argon purge gas flow was stopped for atomization. Peak areas were recorded on a Perkin Elmer PRS-10 printer sequencer.

The ICP-MS measurements were made on a Sciex ICP-MS. Plasma flow was 12 L/min., auxilliary flow was 1.4 L/min., and nebulizer flow was 1.1 L/ min. The plasma was run at 1250 W and 27.1 MHz. The mass spectrometer was scanned from 27.5 to 28.5 amu in 0.1 mass units. Each mass was scanned for 0.5 sec and each mass peak was scanned eight times.

6.2.2 Sample Drying and Mixing

Four bottles each of Bran, Flour, Gluten, Whole Egg Powder, Whole Milk Powder, Meat, Starch and Cellulose were obtained from Agriculture Canada, Ottawa through Dr. Milan Ihnat. One bottle each of Corn Kernel and Corn Stalk were purchased from the National Institute for Science and Technology, Gaithersburg, M.D., USA 20899. All bottles were tumbled end-over-end for at least 2 hours prior to removal of material. After tumbling, about 5-g portions were transferred to clean, dry glass weighing bottles and dried at 85°C for 4 hours.

6.2.3 Sample Preparation for GFAAS

Approximately 0.25 g samples of Corn Stalk, 0.075 g samples of Whole Egg Powder and 0.5 g samples of the remaining materials were weighed to the nearest 0.1 mg into platinum crucibles. The crucibles were placed in a muffle oven and heated at 200°C for 1 hour, then 400°C for 1 hour and finally 600°C for 4 hours to ash the samples. After cooling, 1 g of Na_2CO_3 was mixed with the ash and the mixture fused over a Meker burner for 3 minutes. The solid was dissolved in 10 mL of deionized water and 1 mL of 10% HCl. The solution was transferred to a 50-mL volumetric flask and diluted to volume with deionized water.

For analysis, the method of Nater and Burau (150) was followed. Ten mL of sample solution was placed in a 60-mL polyethylene bottle and 1 mL of 0.2 M KF/0.2 M HF matrix modifier was added. The bottles were tightly capped and placed in an oven at 70° C for 4 hours, then allowed to cool to room temperature prior to measurement.

6.2.4 Sample Preparation for ICP-MS

Samples were dry ashed, fused with Na_2CO_3 and diluted to 50 mL as in section 6.2.3. Prior to running the samples on the ICP-MS they were diluted 1/10 to prevent nebulizer blockage from the high salt content of the solutions.

6.2.5 Standards

Working standards were prepared by pipetting appropriate volumes of a 1000 μg/mL Si stock solution (Spex Industries) and diluting to 50 mL. All solutions were stored in polyethylene volumetric flasks (Nalgene Labware).

Standard reference materials used were NIST 1572 Citrus Leaves, NIST 1573 Tomato Leaves, NIST 1575 Pine Needles, and NIST 1566 Oyster Tissue.

6.3 RESULTS AND DISCUSSION

Use of a KF/HF matrix modifier in the graphite furnace produces an alkali metal hexafluoride which can undergo thermal decomposition to give the metal fluoride and silicon tetrafluoride (150). In this way the silicon is separated from the carbon surface before carbide formation can occur. The pretreatment of graphite tubes and platforms with zirconium was carried out to form zirconium carbide on the graphite surface thereby decreasing the formation of silicon carbide.

The results of the furnace analyses are given in Table 6.1. It can be seen that no reproducible results were obtained. Samples were not reproducible from day to day, sample to sample or even from injection to injection. The poor results may be due to the high salt content from the Na_2CO_3 present. Nater and Burau did trials only on aqueous standards and reported good reproducibility and good detection limits (150). The detection limit that was achieved in this work was about 1 ppm Si, far above the 2.7 ppb obtained by Nater and Burau. To check the method, a series of aqueous standards without Na_2CO_3 were run, but no improvement was observed in either reproducibility or detection limit.

Standard reference materials prepared in the same way gave low results compared to the certified values. This, combined with the fact that about only one quarter of the digested samples gave any absorbance reading at all, resulted in the method being abandoned.

The results of the ICP-MS analyses are given in Table 6.2. All readings are the result of only one subsample (except Oyster Tissue where two subsamples were run). Eight readings were taken on each subsample. The silicon concentrations were determined from an aqueous silicon calibration plot. The calibration curve was linear from 0 to 1.0 ppm Si but leveled off at 1.5 ppm. The detection limit was 0.2 ppm Si.

The silicon concentrations found in standard reference materials by ICP-MS were not within an acceptable range of certified values, but tended to be high. However, they agree much better than the GFAAS results. A major problem with the ICP-MS method is interference of N_2^+ on the silicon peak at 28 amu. To remove or decrease the interference would require considerable effort to eliminate introduction of atmospheric nitrogen into the mass spectrometer from the plasma. At this point it was decided not to continue with this approach for the determination of silicon.

Table 6.1 Results of Silicon Analyses by GFAAS.

Flour	Gluten	Whole Egg Powder	Corn Stalk
68	264	3255	1713
183	139	3799	546
	152		609
	176		162
			130

	1572 Tomato Leaves	1573 Citrus Leaves	1575 Pine Needles	1566 Oyster Tissue
	4050	3930	249	282
	3966	1362		208
	3718	521		
Cert. Value	(3000)	(1900)	(814)	(1100)

Table 6.2 Results of Silicon Analyses by ICP-MS.

Sample	Si Conc, µg/g	Certified Value
Flour	145 ± 86	
Gluten	176 ± 130	
Egg Powder	3364 ± 667	
Corn Kernel	88 ± 72	
Corn Stalk	1869 ± 217	
1572 Citrus Leaves	1686 ± 290	(1900)
1573 Tomato Leaves	8022 ± 948	(3000)
1575 Pine Needles	1559 ± 302	(814)
1566 Oyster Tissue	1608 ± 175	(1100)

CHAPTER 7

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 SUMMARY

During the course of this work aluminum at trace levels was determined in 10 agricultural materials. Two analytical techniques were used, graphite furnace atomic absorption spectroscopy (GFAAS) and neutron activation analysis (INAA). Phosphorus was also determined in the agricultural materials by derivative activation analysis in order to correct for the phosphorus interference on the aluminum values obtained by INAA. The correction brought the two sets of aluminum data into close agreement for those samples where silicon was absent. Silicon also interferes with aluminum values obtained by INAA. In this study GFAAS and inductively coupled plasma mass spectrometry (ICP-MS) were investigated for the determination of silicon values, but neither was successful.

7.2 SUGGESTIONS FOR FUTURE WORK

An alternate method for aluminum analysis could be the direct use of inductively coupled plasma mass spectrometry (ICP-MS). Conventional ICP atomic emission spectrometry is not sensitive enough but the added sensitivity of the mass spectrometer may make it possible to get reliable aluminum values.

In order to determine silicon by ICP-MS it is necessary to reduce atmospheric nitrogen entry and thereby decrease interference from the N_2^+ peak. This might be done in several ways. These include changing the position of the plasma torch to decrease air entrainment, moving the torch closer to the MS sample entry, or purging the sample solutions with argon prior to nebulization.

Another area of study could be the determination of both silicon and phosphorus in a single sample. The silicon could be distilled off as SiF_4 and trapped in a solution containing molybdate and vanadate compounds. The silicomolybdate complex could then be extracted into an organic solvent such as methylisobutyl ketone and the silicon

determined indirectly by INAA by measurement of the vanadium peak. The solution from which the silicon was distilled could then be used to determine phosphorus by the procedure described in Chapter 5, that is, phosphorus could be complexed as the phosphovanadomolybdate, extracted into an organic solvent, irradiated, and the vanadium measured as was done in this work. This method would separate the silicon and phosphorus before extraction, thereby eliminating the interference that each element has on the other when forming heteropoly acids. Control of the pH would be necessary to ensure that the complexes are formed quantitatively. This method would require not only careful control of pH, but also careful trapping of the silicon to prevent losses.

7.3 CONCLUSIONS

To determine aluminum in biological materials GFAAS is the best method providing that the sample is not needed for further analyses. GFAAS is sensitive and the technique is rapid if a simple quick, sample dissolution procedure such as microwave dissolution is available. INAA is also sensitive and rapid and may be used if the sample should not be destroyed. However, the phosphorus and silicon contents of the sample must be known if useful data are to be obtained by INAA.

Phosphorus in biological materials may be determined by DAA since it is reliable and sensitive. This method cannot be used to obtain phosphorus measurements for the correction of aluminum values obtained by INAA if the aluminum content is less than 2 μg/g and the P:Al ratio is greater than about 5000.

Silicon is very difficult to determine at trace levels. GFAAS is not reliable and other techniques such as ICP-AES and ICP-MS suffer from interferences.

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APPENDIX 1

This appendix contains the data file for the Statworks program for aluminum by GFAAS. Also included are the descriptive statistics (average, standard deviation etc.) and F ratio calculations for each material.

StatWorks™ Data

Al by AA

	FLOUR BOT#	FLOUR	GLUTEN BOT#	GLUTEN	BRAN BOT#	BRAN
1	488	13 77	532	11 35	312	1 53
2	488		532	12 22	312	1 39
3	488	13 93	532	10 64	312	1 22
4	488	13 24	532	10 21	390	1 50
5	640	13 46	639	10 33	390	1 09
6	640	13 98	639	10 39	390	2 02
7	640	11 23	639	11 57	390	1 23
8	640	12 64	639	11 31	927	1 40
9	935	11 39	1288	11 86	927	1 15
10	935	14 00	1288	12 33	927	1 06
11	935	14 62	1288	11 88	927	1 53
12	935	12 50	1288	8 29	927	1 83
13	971	16 25	1328	10 29	1428	1 33
14	971	14 32	1328	12 74	1428	1 02
15	971	12 70	1328	9 90	1428	1 48
16	971	11 43	1328	9 72	1428	1 52
17	971	12 88				
18	971	12 80				
19						

	WEP BOT#	WEP	MEAT BOT#	MEAT	CELL BOT#	CELL
1	329	549	57	.989	479	3.65
2	329	482	57	.865	479	3.56
3	329	494	57	1.63	479	4 34
4	329	530	57	669	479	3.06
5	512	462	57	1.07	497	3.63
6	512	435	422	.678	497	3.11
7	512	546	422	1.30	497	3.23
8	512	443	422	.728	497	4.94
9	751	484	422	1.21	662	3 87
10	751	544	422	.822	662	4.25
11	751	526	1817	.906	662	4 45
12	751	445	1817	1.14	662	4.43
13	1930	497	1817	1.03	1791	2.88
14	1930	543	1817	1.09	1791	3.36
15	1930	498	3019	1.42	1791	3.11
16	1930	513	3019	.824	1791	4.73
17			3019	.981		
18			3019	.605		
19			3019	.682		

	STCH BOT#	STCH	CORN KERNEL	CORN STALK	WMP
1	140	1.80	4.00	80.18	0.232
2	140	2.30	3.96	70.19	0.226
3	140	2.78	3.88	76.10	0.918
4	140	2.35	3.66	69.58	0.356
5	412	2.64	3.50	78.03	0.314
6	412	1.45	4.44	79.92	0.585
7	412	1.56			0.628
8	412	2.65			0.317
9	869	1.43			0.833
10	869	1.79			0.296
11	869	2.07			0.259
12	869	2.21			0 333
13	1591	3 18			0.402
14	1591	2.90			
15	1591	2.57			
16	1591	1 62			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: FLOUR Observations: 17

Minimum: 11.230	Maximum: 16.250
Range: 5.020	Median: 13.240
Mean: 13.244	Standard Error: 0.311
Variance:	1.645
Standard Deviation:	1.283
Coefficient of Variation:	9.685
Skewness: 0.367	Kurtosis: 0.623

StatWorks™ Data ANOVA Table

Data File: Al by AA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between FLOUR BOT#	1.374	3	0.458	0.239	0.868
Error	24.948	13	1.919		
Total	26.322	16			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: GLUTEN		Observations: 16	
Minimum: 8.290		Maximum: 12.740	
Range: 4.450		Median: 10.975	
Mean: 10.939	Standard Error: 0.293		
Variance:	1.370		
Standard Deviation:	1.171		
Coefficient of Variation:	10.701		
Skewness: -0.475		Kurtosis: 0.111	

StatWorks™ Data ANOVA Table

Data File: Al by AA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between GLUTEN BOT#	0.513	3	0.171	0.102	0.956
Error	20.042	12	1.670		
Total	20.555	15			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: BRAN Observations: 16

Minimum: 1.020	Maximum: 2.020
Range: 1.000	Median: 1.395
Mean: 1.394	Standard Error: 0.068
Variance:	0.075
Standard Deviation:	0.273
Coefficient of Variation:	19.590
Skewness: 0.733	Kurtosis: 0.536

StatWorks™ Data ANOVA Table

Data File: Al by AA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between BRAN BOT#	0.031	3	0.010	0.113	0.950
Error	1.087	12	0.091		
Total	1.118	15			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: WEP Observations: 16

Minimum:	435.000	Maximum:	549.000
Range:	114.000	Median:	497.500
Mean:	499.438	Standard Error:	9.707
Variance:		1507.596	
Standard Deviation:		38.828	
Coefficient of Variation:		7.774	
Skewness:	-0.295	Kurtosis:	-1.168

StatWorks™ Data ANOVA Table

Data File: Al by AA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between WEP BOT#	4650.688	3	1550.229	1.036	0.413
Error	17963.250	12	1496.937		
Total	22613.938	15			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: WMP	Observations: 13
Minimum: 0.226	Maximum: 0.918
Range: 0.692	Median: 0.333
Mean: 0.438	Standard Error: 0.064
Variance:	0.053
Standard Deviation:	0.230
Coefficient of Variation:	52.382
Skewness: 1.214	Kurtosis: 0.280

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: MEAT	Observations: 19
Minimum: 0.605	Maximum: 1.630
Range: 1.025	Median: 0.981
Mean: 0.982	Standard Error: 0.063
Variance:	0.076
Standard Deviation:	0.275
Coefficient of Variation:	28.035
Skewness: 0.716	Kurtosis: 0.193

StatWorks™ Data ANOVA Table

Data File: Al by AA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between MEAT BOT#	0.074	3	0.025	0.286	0.835
Error	1.290	15	0.086		
Total	1.364	18			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: CELL Observations: 16

Minimum: 2.880	Maximum: 4.940
Range: 2.060	Median: 3.640
Mean: 3.787	Standard Error: 0.164
Variance:	0.430
Standard Deviation:	0.656
Coefficient of Variation:	17.319
Skewness: 0.315	Kurtosis: -1.250

StatWorks™ Data ANOVA Table

Data File: Al by AA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between CELL BOT#	1.229	3	0.410	0.941	0.547
Error	5.225	12	0.435		
Total	6.454	15			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: STCH Observations: 16

Minimum: 1.430	Maximum: 3.180
Range: 1.750	Median: 2.255
Mean: 2.205	Standard Error: 0.138
Variance:	0.305
Standard Deviation:	0.552
Coefficient of Variation:	25.048
Skewness: 0.069	Kurtosis: -1.184

StatWorks™ Data ANOVA Table

Data File: Al by AA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between STCH BOT#	1.067	3	0.356	1.216	0.346
Error	3.509	12	0.292		
Total	4.576	15			

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: CORN KERNEL Observations: 6

Minimum: 3.500	Maximum: 4.440
Range: 0.940	Median: 3.920
Mean: 3.907	Standard Error: 0.132
Variance:	0.105
Standard Deviation:	0.323
Coefficient of Variation:	8.278
Skewness: 0.624	Kurtosis: 0.920

StatWorks™ Data Descriptive Statistics

Data File: Al by AA

Variable: CORN STALK Observations: 6

Minimum: 69.580	Maximum: 80.180
Range: 10.600	Median: 77.065
Mean: 75.667	Standard Error: 1.926
Variance:	22.255
Standard Deviation:	4.718
Coefficient of Variation:	6.235
Skewness: -0.593	Kurtosis: -1.946

APPENDIX 2

This appendix contains the data for calculation of aluminum concentrations from area counts for aluminum by neutron activation analysis. The columns on pages 101 to 112 contain the following information:

Sample	sample being determined.
Count time	total count time for gamma ray counting including instrumental correction for dead time.
Pulser Area	pulser count for each sample.
PPUCF	pulse pile up correction factor .
CT/LT	count time divided by live time of 210 s for live time /dead time correction.
Peak area	total area counts for each sample.
PPU Cor Area	total area counts after correction for pulse pile up.
$1\text{-}e^{-L*CL}$	calculation of $1\text{-}e^{-\lambda CT}$ for the live time/dead time correction.
0.661412/H1	calculation of $(1\text{-}e^{-\lambda LT})/(1\text{-}e^{-\lambda CT})$ where $1\text{-}e^{-\lambda LT}$ = 0.661412.
Corr Area	peak area corrected for pulse pile up and live time/dead time.
Area-blk	corrected peak area - corrected blank.
$x = (y \pm b)/m$	calculation of µg of aluminum from standard curve where m=slope, b=intercept and x and y are points on the line.
Sample Wt.	weight of sample used in each determination.
µg Al/g	calculation of aluminum concentration in sample.
Count error	error in peak area count as a fraction.
Error*area	error in peak area counts x peak area.
Error in µg/g	final error given as µg Al/g.

Also included are the data file for the Statworks program, descriptive statistics for each material and F ratio calculations.

StatWorks™ Data

Al by INAA

	FLOUR BOT#	FLOUR	GLUTEN BOT#	GLUTEN	BRAN BOT#	BRAN
1	488	19.03	532	13.13	312	753
2	488	18.32	532	13.53	312	838
3	488	20.28	639	13.87	312	703
4	640	20.38	639	14.87	390	1 268
5	640	18.13	639	17.76	390	921
6	935	17.38	1288	14.15	927	398
7	935	18.29	1288	15.41	927	566
8	971	17.94	1328	13.55	1428	520
9	971	18.75	1328	12.99	1428	828

	WEP BOT#	WEP	MEAT	WMP BOT#	WMP	CELL BOT#
1	329	588	13.25	295	12.15	479
2	329	625	14.50	295	15.50	479
3	512	587	14.06	997	5.16	479
4	512	600	15.83	1234	9.85	497
5	512	598	15.32	1234	11.22	497
6	751	584	15.01	1234	3.81	662
7	751	602	15.62	1262	8.95	662
8	1930	599	11.52	1262	13.62	1791
9	1930	594	12.05			1791

	CELL	STCH BOT#	STCH	CORN KERNEL	CORN STALK	MEAT BOT#
1	5.39	140	1.84	7.29	87.38	57
2	4.10	140	1.83	7.02	137.78	57
3	3.60	140	1.82	7.83	93.68	422
4	3.47	412	2.93		96.50	422
5	4.27	412	1.83		117.31	1817
6	4.29	869	2.08			1817
7	3.62	869	1.26			1817
8	3.97	1591	2.59			3019
9	6.93	1591	1.82			3019

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA
Variable: FLOUR Observations: 9

Minimum: 17.380	Maximum: 20.380
Range: 3.000	Median: 18.320
Mean: 18.722	Standard Error: 0.341
Variance:	1.048
Standard Deviation:	1.024
Coefficient of Variation:	5.468
Skewness: 0.766	Kurtosis: -0.362

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between FLOUR BOT#	3.140	3	1.047	0.998	0.533
Error	5.243	5	1.049		
Total	8.383	8			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA
Variable: GLUTEN Observations: 9

Minimum: 12.990	Maximum: 17.760
Range: 4.770	Median: 13.870
Mean: 14.362	Standard Error: 0.499
Variance:	2.243
Standard Deviation:	1.498
Coefficient of Variation:	10.427
Skewness: 1.666	Kurtosis: 2.958

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between GLUTEN BOT#	8.750	3	2.917	1.586	0.303
Error	9.192	5	1.838		
Total	17.942	8			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA

Variable: BRAN Observations: 9

Minimum: 0.398	Maximum: 1.268
Range: 0.870	Median: 0.753
Mean: 0.755	Standard Error: 0.085
Variance:	0.066
Standard Deviation:	0.256
Coefficient of Variation:	33.899
Skewness: 0.721	Kurtosis: 1.088

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between BRAN BOT#	0.393	3	0.131	4.997	0.058
Error	0.131	5	0.026		
Total	0.524	8			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA

Variable: WEP	Observations: 9
Minimum: 584.000	Maximum: 625.000
Range: 41.000	Median: 598.000
Mean: 597.444	Standard Error: 4.049
Variance:	147.528
Standard Deviation:	12.146
Coefficient of Variation:	2.033
Skewness: 1.488	Kurtosis: 3.178

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between WEP BOT#	223.222	3	74.407	0.389	0.768
Error	957.000	5	191.400		
Total	1180.222	8			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA

Variable: WMP	Observations: 8
Minimum: 3.810	Maximum: 15.500
Range: 11.690	Median: 10.535
Mean: 10.033	Standard Error: 1.416
Variance:	16.046
Standard Deviation:	4.006
Coefficient of Variation:	39.928
Skewness: -0.406	Kurtosis: -0.711

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between WMP BOT#	64.719	3	21.573	1.813	0.284
Error	47.605	4	11.901		
Total	112.324	7			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA

Variable: MEAT	Observations: 9
Minimum: 11.520	Maximum: 15.830
Range: 4.310	Median: 14.500
Mean: 14.129	Standard Error: 0.518
Variance:	2.419
Standard Deviation:	1.555
Coefficient of Variation:	11.009
Skewness: -0.716	Kurtosis: -0.840

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between MEAT BOT#	16.681	3	5.560	10.396	0.015
Error	2.674	5	0.535		
Total	19.355	8			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA

Variable: CELL		Observations: 9	
Minimum:	3.470	Maximum:	6.930
Range:	3.460	Median:	4.100
Mean:	4.404	Standard Error:	0.369
Variance:		1.225	
Standard Deviation:		1.107	
Coefficient of Variation:		25.127	
Skewness:	1.794	Kurtosis:	3.149

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between CELL BOT#	3.167	3	1.056	0.796	0.548
Error	6.631	5	1.326		
Total	9.798	8			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA

Variable: STCH	Observations: 9
Minimum: 1.260	Maximum: 2.930
Range: 1.670	Median: 1.830
Mean: 2.000	Standard Error: 0.163
Variance:	0.239
Standard Deviation:	0.489
Coefficient of Variation:	24.464
Skewness: 0.795	Kurtosis: 0.913

StatWorks™ Data ANOVA Table

Data File: Al by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between STCH BOT#	0.677	3	0.226	0.912	0.501
Error	1.238	5	0.248		
Total	1.915	8			

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA
Variable: CORN KERNEL Observations: 3

Minimum: 7.020	Maximum: 7.830
Range: 0.810	Median: 7.290
Mean: 7.380	Standard Error: 0.238
Variance:	0.170
Standard Deviation:	0.412
Coefficient of Variation:	5.589
Skewness: 0.935	Kurtosis: -NAN'4002'

StatWorks™ Data Descriptive Statistics

Data File: Al by INAA
Variable: CORN STALK Observations: 5

Minimum: 87.380	Maximum: 137.780
Range: 50.400	Median: 96.500
Mean: 106.530	Standard Error: 9.288
Variance:	431.304
Standard Deviation:	20.768
Coefficient of Variation:	19.495
Skewness: 1.006	Kurtosis: -0.346

Sample	Count Time	Pulser Area	PPUCF	CT/LT	Peak Area	PPU Cor Area	1-e(-L*CT)
y = -62.073 + 281.279x							
Blank no flux	214.52	14293	1.064	1.022	23180	24666.651	0.669
Blank std.	212.95	15025	1.005	1.014	1258	1264.143	0.667
1 std.	212.97	15003	1.006	1.014	1496	1505.651	0.667
5 std.	213.01	14846	1.017	1.014	2714	2760.913	0.667
10 std.	213.24	14811	1.021	1.015	4248	4336.318	0.667
20 std.	213.65	14681	1.032	1.017	6597	6806.849	0.668
30 std.	213.89	14576	1.040	1.019	9032	9396.982	0.668
60 std.	215.04	14196	1.074	1.024	16737	17975.593	0.670
F 488 2	214.49	14299	1.064	1.021	6420	6827.925	0.669
F 640 1	214.19	14385	1.056	1.020	6154	6496.795	0.669
F 640 2	214.41	14596	1.042	1.021	5950	6196.986	0.669
F 935 1	214.44	14464	1.051	1.021	5845	6144.043	0.669
F 935 2	214.24	14441	1.052	1.020	6052	6365.823	0.669
F 971 1	214.39	14307	1.062	1.021	5902	6270.577	0.669
F 971 2	214.48	14345	1.060	1.021	6171	6541.753	0.669
B 312 2	213.69	14554	1.041	1.018	1484	1544.856	0.668
B 390 1	213.88	14538	1.043	1.018	1750	1825.391	0.668
B 390 2	213.73	14537	1.042	1.018	1612	1680.382	0.668
B 927 1	213.99	14773	1.027	1.019	1304	1339.229	0.668
B 927 2	213.45	14526	1.042	1.016	1408	1466.916	0.667
B 1428 1	213.83	14746	1.028	1.018	1377	1415.731	0.668
B 1428 2	213.75	14718	1.030	1.018	1530	1575.437	0.668
Stch 140 2	213.20	14927	1.013	1.015	2349	2378.757	0.667
Stch 412 1	213.07	14903	1.014	1.015	2770	2807.894	0.667
Stch 412 2	213.21	14856	1.018	1.015	2155	2192.832	0.667
Stch 869 1	213.16	14840	1.018	1.015	2338	2381.051	0.667
Stch 869 2	213.32	14867	1.017	1.016	1871	1903.419	0.667
Stch 1591 1	213.41	14746	1.026	1.016	2961	3038.305	0.667
Stch 1591 2	213.29	14938	1.012	1.016	2119	2145.168	0.667
Blank	212.28	15140	0.994	1.011		0.000	0.665

0.661412/H1	Corr. Area	Area-Blank	x=(y+b)/m	Sample Wt.	µg Al /g	Count Error	Error*Area
0.988	24903.856	23724.856					
0.992	1272.070	93.070					
0.992	1515.157	336.157					
0.992	2778.579	1599.579					
0.992	4366.189	3187.189					
0.991	6859.682	5680.682					
0.990	9474.726	8295.726					
0.987	18168.396	16989.396					
0.988	6893.149	5714.149	20.536	1.013	20.276	0.014	79.998
0.989	6554.699	5375.699	19.332	0.949	20.380	0.015	77.948
0.989	6255.125	5076.125	18.267	1.008	18.126	0.015	73.604
0.989	6202.079	5023.079	18.079	1.040	17.378	0.015	72.835
0.989	6423.239	5244.239	18.865	1.031	18.294	0.014	73.419
0.989	6329.139	5150.139	18.530	1.033	17.944	0.015	74.677
0.988	6604.103	5425.103	19.508	1.040	18.754	0.014	75.951
0.990	1556.979	377.979	1.564	2.227	0.703	0.030	11.339
0.990	1840.454	661.454	2.572	2.029	1.268	0.027	17.529
0.990	1693.711	514.711	2.051	2.227	0.921	0.028	14.412
0.990	1350.594	171.594	0.831	2.087	0.398	0.033	5.663
0.991	1477.676	298.676	1.283	2.265	0.566	0.030	8.960
0.990	1427.263	248.263	1.103	2.123	0.520	0.031	7.572
0.990	1588.001	409.001	1.675	2.021	0.829	0.029	11.861
0.992	2394.940	1215.940	4.544	2.498	1.819	0.022	26.751
0.992	2826.219	1647.219	6.077	2.076	2.927	0.020	32.944
0.992	2207.797	1028.797	3.878	2.119	1.830	0.024	24.177
0.992	2397.047	1218.047	4.551	2.186	2.082	0.022	26.797
0.991	1916.855	737.855	2.844	2.258	1.260	0.026	18.815
0.991	3060.334	1881.334	6.909	2.663	2.595	0.020	36.686
0.991	2160.173	981.173	3.709	2.035	1.822	0.023	22.567
0.994	0.000	0.000					

Error in μg/g
0.505
0.498
0.482
0.480
0.482
0.486
0.491
0.261
0.283
0.272
0.241
0.253
0.248
0.263
0.316
0.338
0.307
0.316
0.288
0.351
0.301

Sample	Count Time	Pulser Area	PPUCF	CT/LT	Peak Area	PPU Cor Area	1-e(-L*CT)
Blank	212.72	15139	0.996	1.013		0.000	0.666
Cell 479 1	213.04	14882	1.015	1.014	3329	3378.827	0.667
Cell 479 2	213.20	14938	1.012	1.015	2939	2974.039	0.667
Cell 497 2	213.28	14825	1.020	1.016	2985	3044.753	0.667
Cell 662 1	213.25	14955	1.011	1.015	2972	3004.718	0.667
Cell 662 2	213.24	14968	1.010	1.015	2664	2690.862	0.667
Cell 1791 1	213.22	14898	1.015	1.015	2864	2906.199	0.667
Cell 1791 2	213.14	14885	1.015	1.015	4182	4245.731	0.667
G 532 1	216.42	12978	1.182	1.031	4344	5136.080	0.672
G 532 2	217.13	13584	1.133	1.034	4428	5018.248	0.674
G 639 1	217.00	13225	1.163	1.033	4521	5259.578	0.673
G 639 2	217.39	12537	1.229	1.035	5077	6241.737	0.674
G 1288 1	217.33	13140	1.173	1.035	4470	5241.845	0.674
G 1288 2	217.32	12497	1.233	1.035	4566	5629.660	0.674
G 1328 1	217.48	12660	1.218	1.036	4320	5261.647	0.674
G 1328 2	217.07	13173	1.168	1.034	3997	4669.836	0.674
Meat 57 1	218.99	11986	1.295	1.043	6506	8427.843	0.677
Meat 57 2	219.47	11652	1.335	1.045	7010	9361.492	0.678
Meat 422 1	219.03	12149	1.278	1.043	6955	8890.221	0.677
Meat 422 2	219.26	11503	1.351	1.044	7307	9875.060	0.677
Meat 1817 1	219.32	11693	1.330	1.044	7453	9911.417	0.677
Meat 1817 2	219.49	11065	1.406	1.045	6770	9521.478	0.678
Meat 3019 1	219.17	12368	1.256	1.044	6007	7547.300	0.677
Meat 3019 2	219.28	11955	1.300	1.044	6106	7940.697	0.677
C.S. 1	214.06	14364	1.057	1.019	7819	8261.591	0.668
C.S. 2	214.32	14546	1.045	1.021	8974	9374.704	0.669
C.S. 3	214.24	14575	1.042	1.020	8309	8659.506	0.669
C.S. 4	214.29	14287	1.063	1.020	8333	8861.650	0.669
C.S. 5	214.42	14341	1.060	1.021	10384	11007.860	0.669
C.K. 1	214.43	14578	1.043	1.021	4692	4893.256	0.669
C.K. 2	214.74	14304	1.064	1.023	5234	5571.107	0.670

0.661412/H1	Corr. Area	Area-Blank	x=(y+b)/m	Sample Wt.	µg Al /g	Count Error	Error*Area
0.993	0.000	0.000					
0.992	3400.663	2221.663	8.119	1.505	5.394	0.018	39.990
0.992	2994.272	1815.272	6.674	1.628	4.099	0.019	34.490
0.991	3065.986	1886.986	6.929	1.621	4.274	0.019	35.853
0.992	3025.480	1846.480	6.785	1.581	4.292	0.019	35.083
0.992	2709.398	1530.398	5.662	1.565	3.618	0.021	31.373
0.992	2926.094	1747.094	6.432	1.621	3.968	0.020	34.068
0.992	4274.073	3095.073	11.224	1.619	6.931	0.016	49.521
0.984	5206.306	4027.306	14.539	1.107	13.131	0.024	94.642
0.982	5094.481	3915.481	14.141	1.046	13.526	0.024	92.014
0.982	5338.015	4159.015	15.007	1.082	13.873	0.024	99.816
0.981	6340.028	5161.028	18.569	1.046	17.759	0.022	113.543
0.981	5323.718	4144.718	14.956	1.057	14.148	0.023	93.256
0.981	5717.470	4538.470	16.356	1.061	15.413	0.024	106.654
0.981	5345.518	4166.518	15.033	1.110	13.550	0.024	97.913
0.982	4740.177	3561.177	12.881	0.991	12.993	0.024	85.468
0.977	8589.438	7410.438	26.566	2.005	13.249	0.020	144.504
0.976	9550.624	8371.624	29.983	2.068	14.499	0.019	154.875
0.977	9061.445	7882.445	28.244	2.010	14.055	0.018	141.884
0.977	10070.121	8891.121	31.830	2.010	15.834	0.017	151.149
0.977	10108.471	8929.471	31.967	2.086	15.324	0.019	165.195
0.976	9714.250	8535.250	30.565	2.036	15.013	0.019	157.902
0.977	7694.925	6515.925	23.386	2.031	11.516	0.019	120.545
0.977	8097.889	6918.889	24.819	2.059	12.053	0.020	138.378
0.990	8332.935	7153.935	25.654	0.294	87.378	0.013	89.424
0.989	9460.856	8281.856	29.664	0.215	137.781	0.012	95.241
0.989	8737.609	7558.609	27.093	0.289	93.682	0.012	90.703
0.989	8942.521	7763.521	27.821	0.288	96.502	0.012	93.162
0.989	11111.368	9932.368	35.532	0.303	117.306	0.011	104.290
0.989	4939.373	3760.373	13.590	1.863	7.294	0.017	63.926
0.988	5627.296	4448.296	16.035	2.284	7.019	0.011	46.707

Error in µg/g
0.363
0.343
0.348
0.345
0.332
0.342
0.397
0.557
0.548
0.576
0.624
0.552
0.600
0.569
0.525
0.734
0.771
0.725
0.758
0.808
0.782
0.649
0.713
0.539
0.559
0.543
0.552
0.591
0.448
0.387

Sample	Count Time	Pulser Area	PPUCF	CT/LT	Peak Area	PPU Cor Area	1-e(-L*CT)
C.K. 3	214.70	14211	1.071	1.022	5514	5906.450	0.670
C.K. 4	214.58	14513	1.048	1.022	4995	5236.244	0.669
WEP 329 1	214.41	14466	1.051	1.021	16982	17845.872	0.669
WEP 329 2	214.80	14173	1.075	1.023	20618	22154.981	0.670
WEP 512 1	214.58	14406	1.056	1.022	18925	19986.377	0.669
WEP 512 2	215.01	14022	1.087	1.024	22351	24299.538	0.670
WEP 751 1	214.70	14363	1.060	1.022	17765	18828.012	0.670
WEP 751 2	215.18	13964	1.093	1.025	24080	26308.792	0.670
WEP 1930 1	214.82	14079	1.082	1.023	19981	21615.858	0.670
WEP 1930 2	214.85	14065	1.083	1.023	20718	22438.603	0.670
Blank no flux	212.70	15031	1.003	1.013		0.000	0.666
Blank	212.49	15042	1.002	1.012	1079	1080.704	0.666
F 488 1	214.48	14310	1.063	1.021	6282	6675.710	0.669
B 312 1	213.96	14543	1.043	1.019	1471	1534.418	0.668
Cell. 497 1	213.24	14947	1.012	1.015	2622	2652.160	0.667
Stch 140 1	213.33	14824	1.020	1.016	2168	2212.066	0.667
B.L 1	222.75	10206	1.547	1.061	8566	13255.392	0.683
B.L. 2	222.45	11281	1.398	1.059	8289	11588.823	0.682
W.F. 1	214.42	14443	1.053	1.021	3855	4057.744	0.669
W.F. 2	214.52	14322	1.062	1.022	3903	4144.909	0.669
C.L. 1	215.55	13739	1.112	1.026	13611	15140.329	0.671
C.L. 2	215.65	13498	1.133	1.027	13641	15451.783	0.671
D.L. 1	227.86	6112	2.643	1.085	4328	11439.956	0.691
D.L. 2	228.19	7979	2.028	1.087	4310	8739.323	0.692
D.M. 1	228.68	5158	3.143	1.089	5180	16282.795	0.693
D.M. 2	227.93	7842	2.061	1.085	4980	10262.575	0.691
P.N. 1	215.76	14119	1.083	1.027	17580	19047.511	0.671
P.N. 2	215.60	13813	1.107	1.027	16783	18573.027	0.671
WMP 295 1	232.18	4070	4.045	1.106	1997	8077.200	0.698
WMP 295 2	232.93	4702	3.512	1.109	2772	9736.175	0.699
WMP 997 1	232.57	6734	2.449	1.107	1600	3917.896	0.699

0.661412/H1	Corr. Area	Area-Blank	x=(y+b)/m	Sample Wt.	µg Al /g	Count Error	Error*Area
0.988	5965.517	4786.517	17.238	2.201	7.834	0.016	74.191
0.988	5287.268	4108.268	14.826	2.121	6.990	0.017	67.786
0.989	18013.299	16834.299	60.070	0.102	587.767	0.008	134.674
0.988	22381.266	21202.266	75.599	0.121	624.783	0.008	159.017
0.988	20181.132	19002.132	67.777	0.115	587.321	0.008	142.516
0.987	24558.614	23379.614	83.340	0.139	598.274	0.007	163.657
0.988	19016.299	17837.299	63.636	0.109	583.813	0.008	142.698
0.987	26598.836	25419.836	90.593	0.150	602.347	0.007	177.939
0.988	21837.558	20658.558	73.666	0.123	599.396	0.008	154.939
0.988	22670.178	21491.178	76.626	0.129	593.999	0.008	161.184
0.993	0.000	0.000					
0.994	1086.423	0.000					
0.988	6739.337	5560.337	19.989	1.050	19.030	0.014	77.845
0.990	1547.341	368.341	1.530	2.032	0.753	0.030	10.866
0.992	2670.429	1491.429	5.523	1.593	3.467	0.021	31.320
0.991	2227.728	1048.728	3.949	2.142	1.844	0.023	24.121
0.968	13616.608	12437.608	44.439	2.239	19.845	0.019	230.096
0.969	11897.141	10718.141	38.326	2.245	17.069	0.019	203.645
0.989	4095.899	2916.899	10.591	1.551	6.828	0.019	53.963
0.988	4184.768	3005.768	10.907	1.627	6.704	0.020	58.612
0.986	15319.204	14140.204	50.492	0.555	91.042	0.010	134.332
0.986	15637.638	14458.638	51.624	0.566	91.240	0.010	137.357
0.957	11877.884	10698.884	38.257	1.542	24.809	0.040	422.606
0.956	9080.112	7901.112	28.311	1.544	18.332	0.039	304.193
0.955	16935.023	15756.023	56.236	1.097	51.273	0.032	496.315
0.957	10656.987	9477.987	33.917	1.062	31.952	0.033	308.035
0.985	19281.089	18102.089	64.577	0.111	583.352	0.008	144.817
0.986	18794.441	17615.441	62.847	0.105	601.406	0.009	149.731
0.948	8462.106	7283.106	26.114	2.149	12.150	0.009	66.276
0.946	10216.025	9037.025	32.349	2.086	15.505	0.006	57.837
0.947	4107.921	2928.921	10.634	2.059	5.164	0.112	326.575

Error in µg/g
0.484
0.462
0.699
0.786
0.727
0.803
0.728
0.853
0.772
0.794
0.497
0.259
0.332
0.306
1.039
0.945
0.413
0.429
0.698
0.709
1.723
1.302
1.985
1.316
0.736
0.753
0.456
0.426
1.382

Sample	Count Time	Pulser Area	PPUCF	CT/LT	Peak Area	PPU Cor Area	1-e(-L*CT)
WMP 997 2	232.75	6317	2.612	1.108		0.000	0.699
WMP 1234 1	232.08	5541	2.970	1.105	2201	6536.149	0.698
WMP 1234 2	233.08	5056	3.269	1.110	1007	3291.393	0.699
WMP 1262 1	231.81	5656	2.906	1.104	2050	5957.019	0.697
WMP 1262 2	232.32	4211	3.912	1.106	2204	8621.152	0.698
Blank	212.95	15040	1.004	1.014	1238	1242.804	0.667
Blank std.	212.96	15026	1.005	1.014	1688	1696.209	0.667
90 std.	215.01	13947	1.093	1.024	25180	27522.377	0.670
120 std.	215.49	14121	1.082	1.026	32316	34964.847	0.671
150 std.	216.15	13286	1.153	1.029	40535	46756.665	0.672
F 488 1	214.50	14574	1.044	1.021	6266	6538.698	0.669
G 639 1	217.37	12766	1.207	1.035	4658	5623.369	0.674
Bran 312 1	213.95	14747	1.029	1.019	1607	1653.015	0.668
WEP 512 1	214.64	14232	1.069	1.022	19141	20467.354	0.669
Cell 479 2	213.20	14948	1.011	1.015	2787	2818.340	0.667
Stch 140 1	213.33	15021	1.007	1.016	2257	2272.673	0.667
C. S. 5	214.40	14307	1.062	1.021	10341	10987.303	0.669
C. K. 3	214.70	14127	1.078	1.022	5565	5996.525	0.670
Wht. Flr 3	214.63	14442	1.054	1.022	4952	5217.904	0.669
D. M. 3	228.47	7371	2.198	1.088	4703	10335.467	0.692
Pepperbush 1	216.83	13508	1.138	1.033	11475	13059.705	0.673
Pepperbush 2	216.77	14108	1.089	1.032	10538	11480.063	0.673
TORT-1 3	228.16	6424	2.518	1.086	2762	6955.206	0.692
TORT-1 4	227.29	7929	2.032	1.082	2068	4203.052	0.690
Meat 1817 2	219.51	11614	1.340	1.045	7571	10145.608	0.678
WMP 1234 1	232.26	5551	2.967	1.106	2482	7363.043	0.698

0.661412/H1	Corr. Area	Area-Blank	x=(y+b)/m	Sample Wt.	µg Al/g	Count Error	Error*Area
0.946	0.000	0.000	0.221	2.074	0.106		
0.948	6846.198	5667.198	20.369	2.068	9.850	0.019	104.843
0.946	3454.685	2275.685	8.311	2.182	3.810	0.139	315.182
0.948	6236.099	5057.099	18.200	2.033	8.954	0.076	381.811
0.947	9034.605	7855.605	28.149	2.066	13.623	0.080	624.521
0.992	1250.598	0.598					
0.992	1706.882	0.000					
0.987	27815.815	26108.815	93.042				
0.986	35373.459	33666.459	119.911				
0.984	47368.995	45661.995	162.558				
0.988	6601.298	5351.298	19.246	1.050	18.322	0.014	74.918
0.981	5711.683	4461.683	16.083	1.082	14.868	0.023	100.388
0.990	1666.902	416.902	1.703	2.032	0.838	0.028	11.465
0.988	20669.416	19419.416	69.260	0.115	600.177	0.008	145.646
0.992	2837.514	1587.514	5.865	1.628	3.602	0.020	31.750
0.991	2288.764	1038.764	3.914	2.142	1.827	0.023	23.372
0.989	11090.150	9840.150	35.204	0.303	116.224	0.011	103.322
0.988	6056.492	4806.492	17.309	2.201	7.866	0.016	74.501
0.988	5269.306	4019.306	14.510	1.719	8.440	0.017	66.319
0.956	10744.765	9494.765	33.976	1.098	30.938	0.016	151.916
0.983	13249.719	11999.719	42.882	0.065	663.807	0.011	131.997
0.983	11645.621	10395.621	37.179	0.063	586.421	0.011	109.154
0.956	7225.972	5975.972	21.466	0.232	92.647	0.057	340.630
0.958	4358.763	3108.763	11.273	0.216	52.311	0.061	188.080
0.976	10351.452	9101.452	32.578	2.086	15.617	0.018	159.275
0.947	7715.198	6465.198	23.206	2.068	11.222	0.071	455.796

Error in µg/g
0.221
0.593
1.341
1.578
2.441
0.221
0.221
0.221
0.487
0.578
0.261
0.738
0.334
0.304
0.588
0.486
0.456
0.761
0.690
0.609
1.432
0.889
0.787
1.841

APPENDIX 3

This appendix contains calculation of phosphorus concentration from area counts for phosphorus by derivative activation analysis. The columns on pages 123 to 140 contain the following information:

Sample	sample being determined.
Area	total area counts for each sample.
PPUCF	pulse pile up correction factor.
CT	total count time for gamma ray counting including instrumental correction for dead time.
CT/LT	count time divided by live time of 210 s for live time /dead time correction.
0.00308*CT	calculation of λCT.
1-exp(-F1)	calculation of $1-e^{-\lambda CT}$ for the live time/dead time correction.
0.5225/G1	calculation of $(1-e^{-\lambda LT})/(1-e^{-\lambda CT})$ where $1-e^{-\lambda LT}$ = 0.5225.
B1*C1*E1*H1	peak area corrected for pulse pile up and live time/dead time.
Area-blk	corrected peak area - corrected blank.
x = (y±b)/m	calculation of µg of phosphorus from standard curve where m=slope, b=intercept and x and y are points on the line.
Sample Wt.	weight of sample used in each determination.
Area/Wt.	calculation of phosphorus concentration in sample.
P conc, µg/g	final phosphorus concentration after correction for dilution.
% error	error in peak area count as a percent.
Error in µg/g	final error given as µg Al/g.

Also included are the data file for the Statworks program, descriptive statistics for each material and F ratio calculations.

StatWorks™ Data

P by INAA

	FLOUR BOT#	FLOUR	GLUTEN BOT#	GLUTEN	BRAN BOT#	BRAN
1	488	2110	532	1630	312	11?
2	488	2311	532	1615	390	59
3	488	2302	532	1737	390	12?
4	488	2282	532	1528	390	11?
5	488	2314	532	1566	927	5?
6	640	2497	639	1544	927	13?
7	640	2323	639	1571	1428	4?
8	935	2148	639	1485	1428	3?
9	935	2243	639	1518		
10	935	2190	639	1469		
11	935	2284	1288	1726		
12	935	2208	1288	1543		
13	971	2332	1328	1591		
14	971	1986	1328	1447		
15						

	WEP BOT#	WEP	WMP BOT#	WMP	MEAT BOT#	MEAT
1	329	8119	295	6831	57	8194
2	329	8789	295	6861	57	7638
3	512	9585	295	7101	422	8128
4	512	8221	295	7034	422	7642
5	512	7950	295	7064	422	7673
6	512	7803	295	7202	422	7929
7	512	7753	997	7303	422	7709
8	751	8675	997	7167	1817	
9	751	8485	997	7094	1817	7484
10	1930	8033	997	7083	1817	7545
11	1930	8020	997	7066	1817	7713
12	1930	7950	1234	7538	1817	7606
13	1930	8112	1234	6898	3019	7874
14	1930	8031	1262	7428	3019	7494
15			1262	6896		

	STCH BOT#	STCH	CORN KERNEL	CORN STALK
1	140	163	1630	528
2	140	178	1778	549
3	869	169	1720	508
4	869	181	1715	572
5	1591	164	1735	538
6	1591	165		541
7				509

StatWorks™ Data Descriptive Statistics

Data File: P by INAA

Variable: FLOUR Observations: 14

Minimum: 1986.000	Maximum: 2497.000
Range: 511.000	Median: 2283.000
Mean: 2252.143	Standard Error: 32.379
Variance:	14677.824
Standard Deviation:	121.152
Coefficient of Variation:	5.379
Skewness: -0.354	Kurtosis: 1.417

StatWorks™ Data ANOVA Table

Data File: P by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between FLOUR BOT#	74915.714	3	24971.905	2.155	0.156
Error	115896.000	10	11589.600		
Total	190811.714	13			

StatWorks™ Data Descriptive Statistics

Data File: P by INAA

Variable: GLUTEN Observations: 14

Minimum:	1447.000	Maximum:	1737.000
Range:	290.000	Median:	1555.000
Mean:	1569.286	Standard Error:	23.054
Variance:		7440.681	
Standard Deviation:		86.259	
Coefficient of Variation:		5.497	
Skewness:	0.730	Kurtosis:	0.134

StatWorks™ Data ANOVA Table

Data File: P by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between GLUTEN BOT#	37564.357	3	12521.452	2.116	0.161
Error	59164.500	10	5916.450		
Total	96728.857	13			

StatWorks™ Data Descriptive Statistics

Data File: P by INAA

Variable: BRAN Observations: 8

Minimum: 45.000	Maximum: 136.000
Range: 91.000	Median: 114.500
Mean: 97.625	Standard Error: 13.304
Variance:	1415.982
Standard Deviation:	37.630
Coefficient of Variation:	38.545
Skewness: -0.540	Kurtosis: -1.984

StatWorks™ Data ANOVA Table

Data File: P by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between BRAN BOT#	569.208	3	189.736	0.081	0.967
Error	9342.667	4	2335.667		
Total	9911.875	7			

StatWorks™ Data Descriptive Statistics

Data File: P by INAA

Variable: WEP	Observations: 14
Minimum: 7753.000	Maximum: 9585.000
Range: 1832.000	Median: 8072.500
Mean: 8251.857	Standard Error: 130.938
Variance:	240027.824
Standard Deviation:	489.926
Coefficient of Variation:	5.937
Skewness: 1.759	Kurtosis: 3.390

StatWorks™ Data ANOVA Table

Data File: P by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between WEP BOT#	545515.714	3	181838.571	0.706	0.572
Error	2574846.000	10	257484.600		
Total	3120361.714	13			

StatWorks™ Data Descriptive Statistics

Data File: P by INAA

Variable: WMP Observations: 15

Minimum: 6831.000	Maximum: 7538.000
Range: 707.000	Median: 7083.000
Mean: 7104.400	Standard Error: 52.294
Variance:	41019.686
Standard Deviation:	202.533
Coefficient of Variation:	2.851
Skewness: 0.707	Kurtosis: 0.202

StatWorks™ Data ANOVA Table

Data File: P by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between WMP BOT#	87160.900	3	29053.633	0.656	0.598
Error	487114.700	11	44283.155		
Total	574275.600	14			

StatWorks™ Data Descriptive Statistics

Data File: P by INAA

Variable: MEAT	Observations: 13
Minimum: 7484.000	Maximum: 8194.000
Range: 710.000	Median: 7673.000
Mean: 7740.692	Standard Error: 62.969
Variance:	51545.897
Standard Deviation:	227.037
Coefficient of Variation:	2.933
Skewness: 0.976	Kurtosis: 0.036

StatWorks™ Data ANOVA Table

Data File: P by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between MEAT BOT#	190885.969	3	63628.656	1.339	0.322
Error	427664.800	9	47518.311		
Total	618550.769	12			

StatWorks™ Data Descriptive Statistics

Data File: P by INAA

Variable: STCH	Observations: 6
Minimum: 163.000	Maximum: 181.000
Range: 18.000	Median: 167.000
Mean: 170.000	Standard Error: 3.141
Variance:	59.200
Standard Deviation:	7.694
Coefficient of Variation:	4.526
Skewness: 0.763	Kurtosis: -1.644

StatWorks™ Data ANOVA Table

Data File: P by INAA

Source	Sum of Squares	Deg. of Freedom	Mean Squares	F-Ratio	Prob>F
Between STCH BOT#	111.000	2	55.500	0.900	0.505
Error	185.000	3	61.667		
Total	296.000	5			

StatWorks™ Data Descriptive Statistics

Data File: P by INAA
Variable: CORN KERNEL Observations: 5

Minimum: 1630.000	Maximum: 1778.000
Range: 148.000	Median: 1720.000
Mean: 1715.600	Standard Error: 24.101
Variance:	2904.300
Standard Deviation:	53.892
Coefficient of Variation:	3.141
Skewness: -1.003	Kurtosis: 2.224

StatWorks™ Data Descriptive Statistics

Data File: P by INAA
Variable: CORN STALK Observations: 7

Minimum: 508.000	Maximum: 572.000
Range: 64.000	Median: 538.000
Mean: 535.000	Standard Error: 8.541
Variance:	510.667
Standard Deviation:	22.598
Coefficient of Variation:	4.224
Skewness: 0.324	Kurtosis: -0.202

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
y =-1111 + 5057.6x							
25 std	116174	1.0391	269.6	1.123	0.830	0.564	0.926
20 std	93627	1.0312	263.8	1.099	0.813	0.556	0.939
15 std	73217	1.0242	258.6	1.078	0.796	0.549	0.952
10 std	45979	1.0155	252	1.050	0.776	0.540	0.968
15 std	67161	1.0223	257.2	1.072	0.792	0.547	0.955
Blank	116	1.0009	240.7	1.003	0.741	0.524	0.998
Flour 1	11034	1.0047	243.7	1.015	0.751	0.528	0.990
Flour 2		1.0015	241.2	1.005	0.743	0.524	0.997
WEP 1	49493	1.0167	252.9	1.054	0.779	0.541	0.966
WEP 2	51703	1.0174	253.5	1.056	0.781	0.542	0.964
WMP 1	76894	1.0257	259.7	1.082	0.800	0.551	0.949
WMP 2	78644	1.0265	260.3	1.085	0.802	0.551	0.948
Meat 1	79288	1.0263	260.2	1.084	0.801	0.551	0.948
Meat 2	72513	1.0242	258.6	1.078	0.796	0.549	0.952
Bovine Liver 1		1.0282	261.6	1.090	0.806	0.553	0.944
Bovine Liver 2	83317	1.0277	261.2	1.088	0.804	0.553	0.945
5 std	23222	1.0081	246.3	1.026	0.759	0.532	0.983
y = -295.564 + 5004.469x							
TORT-1 SO4	95090	1.0339	265.8	1.108	0.819	0.559	0.935
Bov. Liv. SO4	103258	1.0363	267.6	1.115	0.824	0.561	0.931
Oyst. Tiss. SO4	128265	1.0455	274.3	1.143	0.845	0.570	0.916
Tom. Lea. SO4	94259	1.0332	265.3	1.105	0.817	0.558	0.936
Cit. Lea. SO4	70095	1.0248	259	1.079	0.798	0.550	0.951
Pin. Need.SO4	64571	1.0235	258.1	1.075	0.795	0.548	0.953
Wh. Flr. SO4	73297	1.0264	260.3	1.085	0.802	0.551	0.948
y = 5423.543 + 3387.851x							
25 H2O2	84818	1.0293	262.4	1.093	0.808	0.554	0.943
15 H2O2	55218	1.019	254.7	1.061	0.784	0.544	0.961
10 H2O2	40495	1.0139	250.8	1.045	0.772	0.538	0.971
5 H2O2	20971	1.0086	246	1.025	0.758	0.531	0.984

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
125602.00	125486.00						
99682.83	99566.83						
76887.65	76771.65						
47452.35	47336.35						
70265.43	70149.43						
116.21	0.00		0.2674				
11141.30	11025.30		0.2628				
0.00			0.2602				
51201.14	51085.14		0.2595				
53567.35	53451.35						
80986.29	80870.29						
82960.54	82844.54		0.249				
83612.41	83496.41		0.254				
76148.35	76032.35						
0.00							
88098.64	87982.64						
23609.79	23493.79						
101776.50	101660.50	20.373	0.0514				
111041.21	110925.21	22.224	0.0503				
140401.62	140285.62	28.091	0.0791				
100751.62	100635.62	20.168	0.1264				
73691.67	73575.67	14.761	0.2502				
67716.53	67600.53	13.567	0.2496				
77312.52	77196.52	15.485	0.2528				
89969.46	89390.46	24.785					
57391.35	56812.35	15.169					
41659.57	41080.57	10.525					
21323.16	20744.16	4.522					

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
Blk H2O2	578	1.0013	241	1.004	0.742	0.524	0.997
TORT-1 H2O2	80573	1.0267	260.5	1.085	0.802	0.552	0.947
O.T H2O2	71434	1.0239	258.4	1.077	0.796	0.549	0.952
T.L. H2O2	86255	1.029	262.2	1.093	0.808	0.554	0.943
C.L. H2O2	55209	1.0185	254.3	1.060	0.783	0.543	0.962
P.N. H2O2	50894	1.0172	253.3	1.055	0.780	0.542	0.965
y = -295.564 + 5004.469x							
Flour SO4	85135	1.0298	262.8	1.095	0.809	0.555	0.942
Gluten SO4	68585	1.0249	259.1	1.080	0.798	0.550	0.950
WMP SO4	87347	1.0306	263.4	1.098	0.811	0.556	0.940
WEP SO4	111442	1.0394	269.8	1.124	0.831	0.564	0.926
Meat SO4	104029	1.0368	267.9	1.116	0.825	0.562	0.930
y = 58.6 + 4915.2x							
25 HCLO4	112089	1.045	273.9	1.141	0.844	0.570	0.917
20 HCLO4	92030	1.038	268.8	1.120	0.828	0.563	0.928
15 HCLO4	70537	1.0316	264.1	1.100	0.813	0.557	0.939
10 HCLO4	46433	1.0204	255.7	1.065	0.788	0.545	0.959
5 HCLO4	24384	1.015	251.6	1.048	0.775	0.539	0.969
Blk HCLO4	318	1.0079	246.2	1.026	0.758	0.532	0.983
TORT-1 HCLO4	96461	1.0344	266.2	1.109	0.820	0.560	0.934
B.L. HCLO4	126949	1.0447	273.7	1.140	0.843	0.570	0.917
O.T. HCLO4	87669	1.0312	263.8	1.099	0.813	0.556	0.939
T.L. HCLO4	95899	1.0338	265.7	1.107	0.818	0.559	0.935
C.L. HCLO4	72802	1.0258	259.8	1.083	0.800	0.551	0.949
P.N. HCLO4	64704	1.023	257.7	1.074	0.794	0.548	0.954
y = 296.6 + 4882.42x							
Flour 935 1							
Gluten 1328 1	48954	1.0178	253.8	1.058	0.782	0.542	0.963
WMP 1234 1	90175	1.0316	264.1	1.100	0.813	0.557	0.939
WEP 512 1	115326	1.0405	270.6	1.128	0.833	0.565	0.924
Meat 57 1	95915	1.0335	265.5	1.106	0.818	0.559	0.935

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
579.53	0.00	0.000					
85034.70	84455.70	23.328	0.0507				
74973.22	74394.22	20.358	0.0529				
91442.65	90863.65	25.220	0.1271				
57323.09	56744.09	15.148					
52704.67	52125.67	13.785					
90397.82	90281.82	18.099					
72120.87	72004.87	14.447					
92892.95	92776.95	18.598					
120552.81	120436.81	24.125					
111968.99	111852.99	22.410					
122571.32	122248.32	24.487					
99287.62	98964.62	19.834					
75158.55	74835.55	15.013					
48391.70	48068.70	9.664					
25139.46	24816.46	5.018					
323.20	0.00	0.000					
103348.88	103025.88	20.646	0.0507				
138744.34	138421.34	27.719	0.0505				
93339.46	93016.46	18.646	0.0529				
102618.79	102295.79	20.500	0.1271				
76694.25	76371.25	15.320	0.2525				
67786.57	67463.57	13.540	0.2513				
			0.1291				
50759.59	50291.59	10.240	0.1287	79.563	1591.266	0.5	253.80
96083.22	95615.22	19.523	0.0518	376.888	7537.770	0.3	288.25
125019.20	124551.20	25.449	0.0531	479.273	9585.457	0.3	375.06
102578.78	102110.78	20.853	0.0509	409.690	8193.800	0.3	307.74

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
Bovine Liver 1	134824	1.047	275.3	1.147	0.848	0.572	0.914
Oyster Tissue 1	94862	1.0333	265.4	1.106	0.817	0.558	0.936
Meat 422 1	105525	1.0373	268.1	1.117	0.826	0.562	0.930
WEP 1930 1	97176	1.0344	266.2	1.109	0.820	0.560	0.934
WMP 1262 1	87800	1.0309	263.6	1.098	0.812	0.556	0.940
Gluten 639 1	54443	1.0201	255.5	1.065	0.787	0.545	0.959
Flour 640 1	71325	1.02461	258.9	1.079	0.797	0.550	0.951
Flour 488 1	61015	1.02168	256.7	1.070	0.791	0.546	0.956
Gluten 532 1	50289	1.0188	254.5	1.060	0.784	0.543	0.962
WEP 329 1	97860	1.0353	266.8	1.112	0.822	0.560	0.932
WMP 997 1	87580	1.0305	263.3	1.097	0.811	0.556	0.940
Meat 3019 1	93205	1.0329	265.1	1.105	0.817	0.558	0.936
TORT-1 1	100534	1.0348	266.5	1.110	0.821	0.560	0.933
Tomato Leaves 1	94077	1.0325	264.8	1.103	0.816	0.558	0.937
Meat 1817 1	90792	1.0319	264.3	1.101	0.814	0.557	0.938
WMP 295 1	83773	1.029	262.2	1.093	0.808	0.554	0.943
WEP 751 1	99633	1.035	266.6	1.111	0.821	0.560	0.933
Gluten 1288 1	53089	1.0193	254.9	1.062	0.785	0.544	0.961
Flour 971 1	68664	1.0239	258.4	1.077	0.796	0.549	0.952
20 std	90863	1.0343	266.1	1.109	0.820	0.559	0.934
15 std	70692	1.0301	263	1.096	0.810	0.555	0.941
10 std	48176	1.02168	256.7	1.070	0.791	0.546	0.956
5 std	24009	1.014	250.9	1.045	0.773	0.538	0.971
Blank	463	1.005	243.9	1.016	0.751	0.528	0.989
y = 297.095 + 5221.246x							
Flour 935 2a	72610	1.0248	259	1.079	0.798	0.550	0.951
Gluten 1328 2	48449	1.0174	253.5	1.056	0.781	0.542	0.964
WMP 1234 2	91815	1.032	264.4	1.102	0.814	0.557	0.938
WEP 512 2a	105987	1.037	268.1	1.117	0.826	0.562	0.930
Meat 57 2	115542	1.0413	271.2	1.130	0.835	0.566	0.923
Citrus Leaves 1	64851	1.0239	258.4	1.077	0.796	0.549	0.952

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
147988.98	147520.98	30.154	0.0542	556.346	11126.929	0.3	443.97
101419.48	100951.48	20.616	0.059	349.420	6988.399	0.3	304.26
113664.19	113196.19	23.124	0.0569	406.392	8127.837	0.3	340.99
104114.94	103646.94	21.168	0.0527	401.667	8033.340	0.3	312.34
93426.81	92958.81	18.979	0.0511	371.404	7428.081	0.3	280.28
56707.71	56239.71	11.458	0.1484	77.211	1544.214	0.3	170.12
74960.85	74492.85	15.197	0.1217	124.869	2497.389	0.4	299.84
63753.93	63285.93	12.901	0.1223	105.489	2109.771	0.4	255.02
52244.08	51776.08	10.544	0.1294	81.483	1629.651	0.4	208.98
105022.88	104554.88	21.354	0.0526	405.966	8119.321	0.5	525.11
93119.28	92651.28	18.916	0.0518	365.169	7303.382	0.3	279.36
99569.55	99101.55	20.237	0.0514	393.714	7874.272	0.3	298.71
107797.43	107329.43	21.922	0.0539	406.718	8134.355	0.3	323.39
100422.01	99954.01	20.411	0.1292	157.984	3159.672	0.3	301.27
96794.59	96326.59	19.669	0.0494	398.148	7962.965	0.3	290.38
88811.37	88343.37	18.033	0.0528	341.542	6830.844	0.3	266.43
106866.21	106398.21	21.731	0.0501	433.760	8675.193	0.4	427.46
55209.60	54741.60	11.151	0.1292	86.310	1726.197	0.3	165.63
72065.98	71597.98	14.604	0.1252	116.643	2332.859	0.4	288.26
97328.78	96860.78	19.778				0.3	291.99
75103.90	74635.90	15.226				0.4	300.42
50338.59	49870.59	10.154				0.5	251.69
24705.22	24237.22	4.903				0.7	172.94
467.77	0.00					7.5	35.08
76335.71	75612.71	14.425	0.1286	112.169	2243.380	0.6	458.01
50196.01	49473.01	9.419	0.1302	72.339	1446.777	0.9	451.76
97907.77	97184.77	18.557	0.0538	344.917	6898.335	0.3	293.72
114128.81	113405.81	21.663	0.0527	411.068	8221.351	0.3	342.39
125449.59	124726.59	23.831	0.0624	381.915	7638.293	0.3	376.35
68064.07	67341.07	12.841	0.2509	51.179	1023.571	0.4	272.26

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
Pine Needles1	59847	1.0218	256.8	1.070	0.791	0.547	0.956
Meat 422 2a	95965	1.0332	265.3	1.105	0.817	0.558	0.936
WEP 1930 2a	110423	1.0388	269.4	1.123	0.830	0.564	0.927
WMP 1262 2	87377	1.0301	263	1.096	0.810	0.555	0.941
Gluten 639 2a	53274	1.01889	254.6	1.061	0.784	0.544	0.961
Flour 640 2	74241	1.0256	259.7	1.082	0.800	0.551	0.949
Flour 935 2b	73791	1.0256	259.7	1.082	0.800	0.551	0.949
Gluten 639 2b	50516	1.018	254	1.058	0.782	0.543	0.963
WEP 512 2b	100842	1.0361	267.4	1.114	0.824	0.561	0.931
WEP 1930 2b	111670	1.0388	269.4	1.123	0.830	0.564	0.927
Meat 422 2b	99490	1.0334	265.4	1.106	0.817	0.558	0.936
Flour 488 2a	72773	1.025	259.2	1.080	0.798	0.550	0.950
Gluten 532 2a	53641	1.019	254.7	1.061	0.784	0.544	0.961
WEP 329 2	113324	1.0395	269.9	1.125	0.831	0.565	0.926
WMP 997 2a	91923	1.0315	264.1	1.100	0.813	0.557	0.939
Meat 3019 2	91488	1.0315	264.1	1.100	0.813	0.557	0.939
Wheat Flour 1	66209	1.023	257.7	1.074	0.794	0.548	0.954
Bovine Liver 2	141734	1.04948	277.1	1.155	0.853	0.574	0.910
Meat 1817 2a	96682	1.0335	265.5	1.106	0.818	0.559	0.935
WMP 295 2a	90311	1.03105	263.7	1.099	0.812	0.556	0.940
WEP 751 2	103132	1.0353	266.8	1.112	0.822	0.560	0.932
Gluten 1288 2	50861	1.0184	254.2	1.059	0.783	0.543	0.962
Flour 971 2	63323	1.0226	257.4	1.073	0.793	0.547	0.954
25 std	119704	1.0435	272.8	1.137	0.840	0.568	0.919
20 std	97929	1.0348	266.5	1.110	0.821	0.560	0.933
15 std	76327	1.0293	262.4	1.093	0.808	0.554	0.943
10 std	51349	1.0204	255.7	1.065	0.788	0.545	0.959
5 std	25757	1.013	250.1	1.042	0.770	0.537	0.973
Blank	719	1.0027	242.1	1.009	0.746	0.526	0.994
y = 297.095 + 5221.246x							
Flour 935 1	69952	1.0243	258.7	1.078	0.797	0.549	0.951

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
62549.22	61826.22	11.784	0.2516	46.838	936.762	0.4	250.20
102575.13	101852.13	19.450	0.0509	382.130	7642.609	0.3	307.73
119318.08	118595.08	22.657	0.0565	401.011	8020.225	0.3	357.95
92830.22	92107.22	17.584	0.051	344.785	6895.703	0.3	278.49
55357.44	54634.44	10.407	0.1325	78.544	1570.878	0.4	221.43
78184.48	77461.48	14.779	0.1272	116.187	2323.745	0.4	312.74
77710.58	76987.58	14.688	0.1286	114.217	2284.332	0.4	310.84
52403.55	51680.55	9.841	0.1325	74.274	1485.482	0.5	262.02
108393.32	107670.32	20.565	0.0527	390.223	7804.467	0.3	325.18
120665.54	119942.54	22.915	0.0565	405.579	8111.578	0.3	362.00
106377.69	105654.69	20.179	0.0509	396.439	7928.772	0.5	531.89
76542.48	75819.48	14.465	0.1252	115.531	2310.628	0.4	306.17
55752.28	55029.28	10.483	0.1298	80.760	1615.206	0.4	223.01
122616.76	121893.76	23.289	0.053	439.413	8788.270	0.3	367.85
97936.26	97213.26	18.562	0.0518	358.339	7166.787	0.3	293.81
97472.80	96749.80	18.473	0.0493	374.710	7494.205	0.3	292.42
69363.27	68640.27	13.090	0.2501	52.337	1046.744	0.4	277.45
156314.36	155591.36	29.743	0.0558	533.026	10660.522	0.3	468.94
103399.07	102676.07	19.608	0.0524	374.203	7484.063	0.3	310.20
96125.54	95402.54	18.215	0.0531	343.035	6860.708	0.3	288.38
110680.77	109957.77	21.003	0.0495	424.300	8486.010	0.3	332.04
52796.33	52073.33	9.917	0.1285	77.172	1543.431	0.4	211.19
66287.21	65564.21	12.500	0.1259	99.288	1985.765	0.4	265.15
130519.99	129796.99	24.803				0.3	391.56
105004.22	104281.22	19.916				0.3	315.01
80962.75	80239.75	15.311				0.4	323.85
53515.08	52792.08	10.054				0.5	267.58
26449.32	25726.32	4.870				0.6	158.70
722.98	0.00					5	36.15
73475.96	72700.96	13.867	0.1291	107.414	2148.282	0.4	293.90

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
Flour 935 2A2	70946	1.0249	259.1	1.080	0.798	0.550	0.950
WEP 512 2A2	102839	1.0356	267.1	1.113	0.823	0.561	0.932
Meat 422 2A2	96446	1.0329	265.1	1.105	0.817	0.558	0.936
WEP 1930 2A2	109622	1.0383	269	1.121	0.829	0.563	0.928
Gluten 639 2A2	51606	1.01851	254.3	1.060	0.783	0.543	0.962
Flour 935 2B2	71474	1.02528	259.4	1.081	0.799	0.550	0.950
Gluten 639 2B2	50040	1.0177	253.7	1.057	0.781	0.542	0.964
WEP 512 2B2	100423	1.0351	266.7	1.111	0.821	0.560	0.933
WEP 1930 2B2	110701	1.0384	269.1	1.121	0.829	0.563	0.927
Meat 422 2B2	96866	1.03308	265.2	1.105	0.817	0.558	0.936
Flour 488 2A2	72506	1.025	259.2	1.080	0.798	0.550	0.950
Gluten 532 2A2	53005	1.10889	254.6	1.061	0.784	0.544	0.961
WMP 997 2A2	91069	1.03146	264	1.100	0.813	0.557	0.939
Meat 1817 2A2	97490	1.03363	265.6	1.107	0.818	0.559	0.935
WMP 295 2A2	93318	1.032	264.4	1.102	0.814	0.557	0.938
WMP 295 3A	90009	1.03119	263.8	1.099	0.813	0.556	0.939
TORT -1	99018	1.03485	266.5	1.110	0.821	0.560	0.933
Oyster Tissue 2	85307	1.02944	262.5	1.094	0.809	0.554	0.942
Tomato Leaves 2	93004	1.0324	264.7	1.103	0.815	0.557	0.937
Citrus Leaves 2	73458	1.0258	259.8	1.083	0.800	0.551	0.949
Pine Needles 2	64304	1.023	257.7	1.074	0.794	0.548	0.954
Flour 488 2B1	71900	1.02487	259.1	1.080	0.798	0.550	0.950
Gluten 532 2B1	50968	1.01798	253.9	1.058	0.782	0.543	0.963
WMP 295 3B1	90334	1.03146	264	1.100	0.813	0.557	0.939
WMP 997 2B1	90946	1.03132	263.9	1.100	0.813	0.556	0.939
Meat 1817 2B1	99523	1.03417	266	1.108	0.819	0.559	0.934
Bran 312 1	32186	1.01326	250.3	1.043	0.771	0.537	0.972
Cell 479	140	1.0028	242.2	1.009	0.746	0.526	0.994
Starch 869	829	1.00588	244.6	1.019	0.753	0.529	0.987
Corn Stalk	133295	1.04081	276.1	1.150	0.850	0.573	0.912
Corn Kernel	76636	1.03703	268.1	1.117	0.826	0.562	0.930

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
74603.59	73828.59	14.083	0.1286	109.511	2190.223	0.4	298.41
110442.41	109667.41	20.947	0.0527	397.479	7949.589	0.3	331.33
103031.86	102256.86	19.528	0.0509	383.651	7673.030	0.3	309.10
118332.60	117557.60	22.458	0.0565	397.493	7949.854	0.3	355.00
53582.65	52807.65	10.057	0.1325	75.903	1518.052	0.4	214.33
75216.84	74441.84	14.201	0.1286	110.424	2208.489	0.4	300.87
51873.59	51098.59	9.730	0.1325	73.432	1468.644	0.3	155.62
107738.32	106963.32	20.429	0.0527	387.652	7753.042	0.3	323.21
119524.73	118749.73	22.687	0.0565	401.534	8030.677	0.3	358.57
103512.37	102737.37	19.620	0.0509	385.460	7709.191	0.4	414.05
76261.65	75486.65	14.401	0.1251	115.113	2302.269	0.4	305.05
59943.03	59168.03	11.275	0.1298	86.866	1737.329	0.4	239.77
97009.69	96234.69	18.374	0.0518	354.719	7094.388	0.3	291.03
104290.22	103515.22	19.769	0.0524	377.268	7545.370	0.3	312.87
99510.50	98735.50	18.853	0.0531	355.055	7101.105	0.3	298.53
95829.88	95054.88	18.149	0.0516	351.715	7034.303	0.3	287.49
106177.03	105402.03	20.130	0.0505	398.619	7972.373	0.3	318.53
90512.54	89737.54	17.130	0.0514	333.270	6665.407	0.3	271.54
99253.80	98478.80	18.804	0.1273	147.716	2954.323	0.3	297.76
77385.32	76610.32	14.616	0.2551	57.295	1145.896	0.4	309.54
67367.51	66592.51	12.697	0.2504	50.708	1014.157	0.4	269.47
75604.56	74829.56	14.275	0.1251	114.107	2282.149	0.4	302.42
52864.31	52089.31	9.920	0.1298	76.422	1528.430	0.5	264.32
96226.75	95451.75	18.225	0.0531	343.211	6864.222	0.3	288.68
96852.60	96077.60	18.344	0.0518	354.139	7082.771	0.3	290.56
106577.42	105802.42	20.207	0.0524	385.628	7712.567	0.3	319.73
33068.49	32293.49	6.128	0.2523	24.289	121.445	0.7	231.48
140.81	0.00	0.000	0.259	0.000	0.000	12.3	17.32
839.06	64.06	0.000	0.2558	0.000	0.000	4.7	39.44
145599.88	144824.88	27.681	0.2537	109.108	545.540	0.3	436.80
82525.48	81750.48	15.600	0.2653	58.803	294.014	0.4	330.10

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
Blank	765	1.00614	244.8	1.020	0.754	0.530	0.987
y = -410.81 + 5281.811x							
Flour 488 2b2	72846	1.025	259.3	1.080	0.799	0.550	0.950
Gluten 532 2b2	52119	1.0186	254.4	1.060	0.784	0.543	0.962
WMP 295 2b1	92144	1.0317	264.2	1.101	0.814	0.557	0.938
WMP 295 3b2	92039	1.0317	264.2	1.101	0.814	0.557	0.938
WMP 997 2b2	90719	1.0314	264	1.100	0.813	0.557	0.939
Meat 1817 2b2	98446	1.0347	266.4	1.110	0.821	0.560	0.933
Bran 312 2		1.0059	244.6	1.019	0.753	0.529	0.987
Bran 390 1	190	1.0059	244.6	1.019	0.753	0.529	0.987
Corn Kernel	143451	1.0578	283	1.179	0.872	0.582	0.898
Corn Stalk 1	70887	1.0273	260.9	1.087	0.804	0.552	0.946
Corn Stalk 2	71443	1.02768	261.2	1.088	0.804	0.553	0.945
Bran 927 1	295	1.006	244.7	1.020	0.754	0.529	0.987
Bran 927 2	14995	1.0091	247.1	1.030	0.761	0.533	0.981
Bran 1428 1	71	1.0061	244.8	1.020	0.754	0.530	0.987
Wheat Flour 2	69390	1.02929	262.4	1.093	0.808	0.554	0.943
Bran 390 2	15705	1.0108	248.4	1.035	0.765	0.535	0.977
Bran 1428 2	12092	1.009	246.5	1.027	0.759	0.532	0.982
Corn Stalk 3	64924	1.02565	259.7	1.082	0.800	0.551	0.949
Corn Stalk 4	70887	1.0292	261.6	1.090	0.806	0.553	0.944
Corn Stalk 5	68177	1.028	261.4	1.089	0.805	0.553	0.945
Wheat Flour 1	74826	1.028	261.4	1.089	0.805	0.553	0.945
20 std	96513	1.0343	266.1	1.109	0.820	0.559	0.934
15 std	75970	1.02903	262.2	1.093	0.808	0.554	0.943
10 std	51811	1.02049	255.8	1.066	0.788	0.545	0.958
5 std	26547	1.01313	250.2	1.043	0.771	0.537	0.973
1 std	3424	1.0068	245.3	1.022	0.756	0.530	0.985
Blank	692	1.00268	242.1	1.009	0.746	0.526	0.994
Cellulose	4390	1.01627	252.6	1.053	0.778	0.541	0.966
Starch	5802	1.0385	269.2	1.122	0.829	0.564	0.927

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
774.70	0.00						
76629.51	75934.51	14.454	0.1251	115.543	2310.853	0.6	459.78
54127.34	53432.34	10.194	0.1298	78.537	1570.735	0.4	216.51
98203.84	97508.84	18.539	0.0531	349.134	6982.686	0.3	294.61
98091.94	97396.94	18.518	0.0516	358.873	7177.459	0.3	294.28
96631.24	95936.24	18.241	0.0518	352.148	7042.969	0.3	289.89
105534.32	104839.32	19.927	0.0524	380.284	7605.688	0.3	316.60
192.31	0.00	0.000	0.2583	0.000	0.000	15.8	30.39
160710.21	160015.21	30.373	0.2538	119.674	598.371	0.3	482.13
74896.08	74201.08	14.126	0.1339	105.498	527.490	0.4	299.58
75541.71	74846.71	14.248	0.13	109.603	548.017	0.4	302.17
298.66	0.00	0.000	0.2544	0.000	0.000	11	32.85
15276.98	14581.98	2.839	0.2519	11.269	56.343	0.9	137.49
71.90	0.00	0.000	0.2591	0.000	0.000	51.6	37.10
73603.71	72908.71	13.882	0.0621	223.535	4470.696	0.4	294.41
16055.36	15360.36	2.986	0.2528	11.811	59.057	0.8	128.44
12308.22	11613.22	2.276	0.2542	8.956	44.778	1	123.08
68375.92	67680.92	12.892	0.1269	101.590	507.949	0.4	273.50
75104.79	74409.79	14.166	0.1239	114.332	571.659	0.4	300.42
72130.05	71435.05	13.603	0.1264	107.615	538.074	0.4	288.52
79164.57	78469.57	14.934	0.0647	230.824	4616.490	0.4	316.66
103380.83	102685.83					0.3	310.14
80541.43	79846.43					0.4	322.17
54008.56	53313.56					0.6	324.05
27267.71	26572.71					1.8	490.82
3472.01	2777.01					4.8	166.66
695.82							
4537.76						1.8	81.68
6265.90						2.2	137.85

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
0.5 std	23821	1.03662	267.8	1.116	0.825	0.562	0.930
0.05 std	7363	1.054	280.3	1.168	0.863	0.578	0.904
y = -410.81 + 5281.811x							
Bran 312 3	313	1.0064	245	1.021	0.755	0.530	0.986
Bran 312 4	31329	1.01378	250.7	1.045	0.772	0.538	0.971
Bran 927 3		1.0065	245.1	1.021	0.755	0.530	0.986
Bran 390 3	32545	1.01535	251.9	1.050	0.776	0.540	0.968
Bran 1428 3	126	1.00665	245.2	1.022	0.755	0.530	0.986
Bran 1428 4	33925	1.01509	251.7	1.049	0.775	0.539	0.969
Corn Kernel 6	156621	1.0595	284.2	1.184	0.875	0.583	0.896
Corn Kernel 7	169183	1.06295	286.6	1.194	0.883	0.586	0.891
Corn Kernel 8	170255	1.061	287.4	1.198	0.885	0.587	0.890
Corn Kernel 9	161531	1.0605	284.9	1.187	0.877	0.584	0.894
Bran 927 4	35515	1.0148	251.5	1.048	0.775	0.539	0.969
Bran 390 4	29527	1.01575	252.2	1.051	0.777	0.540	0.967
Corn Kernel 10	149141	1.015747	282.6	1.178	0.870	0.581	0.899
Corn Kernel 11	163964	1.06237	286.2	1.193	0.881	0.586	0.892
25 std	121993	1.04429	273.4	1.139	0.842	0.569	0.918
20 std	98185	1.0351	266.7	1.111	0.821	0.560	0.933
15 std	75233	1.02903	262.2	1.093	0.808	0.554	0.943
10 std	49816	1.01969	255.2	1.063	0.786	0.544	0.960
5 std	26591	1.013	250.1	1.042	0.770	0.537	0.973
Blank	756	1.00255	242	1.008	0.745	0.525	0.994
y = -380.796 + 36300x							
Cell 662 1	2641	1.0395	269.9	1.125	0.831	0.565	0.926
Cell 1791 1	3229	1.03146	264	1.100	0.813	0.557	0.939
Starch 140 1	97252	1.07295	293.5	1.223	0.904	0.595	0.878
Starch 412 1	84422	1.07236	293.1	1.221	0.903	0.595	0.879
Starch 1591 1	221322	1.11585	321.7	1.340	0.991	0.629	0.831
Cell 479 1	2278	1.032	264.4	1.102	0.814	0.557	0.938
Cell 497 1	2527	1.032	264.4	1.102	0.814	0.557	0.938

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
25631.27						0.7	179.42
8190.00						1.8	147.42
317.13	0.00		0.2654	0.000	0.000	11.2	35.52
32221.83	31461.83	6.034	0.2577	23.416	117.082	0.6	193.33
0.00	0.00	0.000	0.2506	0.000	0.000		0.00
33578.40	32818.40	6.291	0.2521	24.955	124.777	0.6	201.47
127.73	0.00	0.000	0.2505	0.000	0.000	25.1	32.06
34983.86	34223.86	6.557	0.2501	26.219	131.095	0.6	209.90
176025.05	175265.05	33.261	0.102	326.084	1630.418	0.3	528.08
191366.55	190606.55	36.165	0.1017	355.606	1778.030	0.2	382.73
192428.31	191668.31	36.366	0.1057	344.051	1720.253	0.2	384.86
181882.42	181122.42	34.370	0.1002	343.009	1715.045	0.3	545.65
36603.19	35843.19	6.864	0.2523	27.205	136.027	0.5	183.02
30488.85	29728.85	5.706	0.2538	22.484	112.418	0.6	182.93
160357.67	159597.67	30.294	0.1051	288.242	1441.211	0.3	481.07
185264.45	184504.45	35.010	0.1009	346.975	1734.877	0.3	555.79
133222.52	132462.52	25.157				0.3	399.67
105337.29	104577.29	19.877				0.3	316.01
79760.08	79000.08	15.035				0.4	319.04
51846.53	51086.53	9.750				0.5	259.23
27305.73	26545.73	5.104				0.6	163.83
759.97	0.00					4.2	31.92
2857.57	0.00	0.000	0.1989	0.000	0.000	3.6	102.87
3439.64	25.64	0.011	0.2975	0.038	0.188	3.1	106.63
112049.82	108635.82	3.003	0.3016	9.958	49.788	0.3	336.15
97163.16	93749.16	2.593	6105	0.000	0.002	0.4	388.65
275099.43	271685.43	7.495	0.2994	25.033	125.166	0.2	550.20
2429.17	0.00	0.000	0.3024	0.000	0.000	3.8	92.31
2694.69	0.00	0.000	0.2003	0.000	0.000	3.5	94.31

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
Cell 662 2	2461	1.0395	269.9	1.125	0.831	0.565	0.926
Starch 869 1	256302	1.13763	335.2	1.397	1.032	0.644	0.812
Starch 140 2	154983	1.06756	289.8	1.208	0.893	0.590	0.885
Starch 412 2		1.02314	257.8	1.074	0.794	0.548	0.954
Cell 497 2	1165	1.017455	253.5	1.056	0.781	0.542	0.964
Cell 1791 2	135	1.02036	255.7	1.065	0.788	0.545	0.959
Cell 479 2	131	1.02089	256.1	1.067	0.789	0.546	0.958
Starch 140 3	145	1.02554	259.6	1.082	0.800	0.550	0.949
Starch 412 3		1.02381	258.3	1.076	0.796	0.549	0.952
Starch 869 2	133	1.02528	259.4	1.081	0.799	0.550	0.950
Cell 1791 2	261	1.03649	267.7	1.115	0.825	0.562	0.930
Starch 1591 2	213	1.0571	282.5	1.177	0.870	0.581	0.899
Cell 1791 3	47	1.019266	254.8	1.062	0.785	0.544	0.961
Starch 1591 3		1.05766	282.9	1.179	0.871	0.582	0.898
0.25 std	11026	1.05497	281	1.171	0.865	0.579	0.902
0.1 std	5825	1.04933	277	1.154	0.853	0.574	0.910
0.075 std	5066	1.04933	277	1.154	0.853	0.574	0.910
0.05 std	4168	1.06165	285.7	1.190	0.880	0.585	0.893
0.025 std	3098	1.0534	279.9	1.166	0.862	0.578	0.904
Blank	3084	1.0514	278.5	1.160	0.858	0.576	0.907
y = -410.81 + 5281.811x							
Corn Kernel 12	54823	1.0222	257.1	1.071	0.792	0.547	0.955
Corn Kernel 13	48449	1.0197	255.2	1.063	0.786	0.544	0.960
Corn Kernel 14	56385	1.0224	257.3	1.072	0.792	0.547	0.955
Corn Kernel 15	48351	1.0197	255.2	1.063	0.786	0.544	0.960
Corn Kernel 16	51987	1.0211	256.3	1.068	0.789	0.546	0.957
Bran 312 5		1.0078	246.1	1.025	0.758	0.531	0.983
Bran 927 5		1.0066	245.1	1.021	0.755	0.530	0.986
Bran 1428 5		1.0078	246.1	1.025	0.758	0.531	0.983
Corn Stalk 6	70990	1.0331	265.2	1.105	0.817	0.558	0.936
Corn Stalk 7	65911	1.0306	263.4	1.098	0.811	0.556	0.940

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
2662.81	0.00	0.000	0.2995	0.000	0.000	3.9	103.85
330479.36	327065.36	9.021	0.3022	29.850	149.248	0.2	660.96
176807.42	173393.42	4.787	0.3135	15.270	76.350	0.3	530.42
0.00	0.00	0.000	0.3042	0.000	0.000		0.00
1207.07	0.00	0.000	3014	0.000	0.000	6.3	76.05
140.69	0.00	0.000	0.3156	0.000	0.000	36.7	51.63
136.66	0.00	0.000	0.3126	0.000	0.000	39.6	54.12
152.67	0.00	0.000	0.3076	0.000	0.000	35.8	54.66
0.00	0.00	0.000	0.3011	0.000	0.000		0.00
139.96	0.00	0.000	0.3023	0.000	0.000	37.5	52.49
280.76	0.00	0.000	3051	0.000	0.000	25.6	71.88
238.31	0.00	0.000	3040	0.000	0.000	34.5	82.22
48.87	0.00	0.000	0.3033	0.000	0.000		0.00
0.00	0.00	0.000	0.3053	0.000	0.000		0.00
12287.06	8873.06	0.255				1.4	172.02
6422.46	3008.46	0.093				2	128.45
5585.61	2171.61	0.070				2.3	128.47
4703.17	1289.17	0.046				3	141.10
3442.18	28.18	0.011				3.5	120.48
3413.79	0.00					3.6	122.90
57343.84	56669.84	10.807	0.138	78.312	1566.235	0.4	229.38
50424.31	49750.31	9.497	0.1268	74.897	1497.942	0.5	252.12
59004.99	58330.99	11.122	0.1311	84.832	1696.648	0.4	236.02
50322.31	49648.31	9.478	0.1277	74.218	1484.361	0.5	251.61
54260.75	53586.75	10.223	0.1294	79.005	1580.109	0.4	217.04
0.00	0.00	0.000	0.2699	0.000	0.000		0.00
0.00	0.00	0.000	0.2684	0.000	0.000		0.00
0.00	0.00	0.000	0.2527	0.000	0.000		0.00
75862.38	75188.38	14.313	0.1322	108.269	541.343	0.4	303.45
70095.91	69421.91	13.221	0.1299	101.781	508.905	0.4	280.38

Sample	Area	PPUCF	CT	CT/LT	.00308*CT	1-EXP(-F1)	.5225/G1
Corn Kernel 18	52046	1.021	256.2	1.068	0.789	0.546	0.957
Bran 927 6		1.0069	245.4	1.023	0.756	0.530	0.985
Blank	670	1.0028	242.2	1.009	0.746	0.526	0.994
y = 860.716 + 26900x							
Starch 140 4	91697	1.0088	309	1.288	0.952	0.614	0.851
Starch 412 4	267	1.0417	271.5	1.131	0.836	0.567	0.922
Starch 869 3	83347	1.069	290.8	1.212	0.896	0.592	0.883
Starch 1591 4	83318	1.0678	290	1.208	0.893	0.591	0.885
Starch 140 5	83006	1.0692	290.9	1.212	0.896	0.592	0.883
Starch 412 5	201	1.0378	268.7	1.120	0.828	0.563	0.928
Starch 869 4	101754	1.0667	289.2	1.205	0.891	0.590	0.886
Starch 1591 5	90820	1.0682	290.3	1.210	0.894	0.591	0.884
1.5 std	38788	1.0499	277.4	1.156	0.854	0.574	0.910
1 std	27581	1.0344	266.2	1.109	0.820	0.560	0.934
0.5 std	17015	1.0261	260	1.083	0.801	0.551	0.948
0.25 std	7690	1.0399	270.2	1.126	0.832	0.565	0.925
0.1 std	6011	1.0271	260.8	1.087	0.803	0.552	0.946
Blank	1816	1.0362	267.5	1.115	0.824	0.561	0.931

B1*C1*E1*H1	Area- blk	x=(y±b)/m	Sample Wt.,g	Area/Wt	P Conc., µg/g	% Error	Error in µg/g
54309.74	53635.74	10.233	0.14	73.090	1461.797	0.4	217.24
			0.2563	0.000	0.000		
673.87	0.00					5.2	35.04
101362.99	99410.99	3.664	0.1026	35.707	178.537	0.4	405.45
290.12	0.00	0.000	0.1082	0.000	0.000	25.9	75.14
95337.17	93385.17	3.440	0.1015	33.887	169.437	0.4	381.35
95097.04	93145.04	3.431	0.1044	32.861	164.303	0.4	380.39
94977.35	93025.35	3.426	0.105	32.630	163.152	0.4	379.91
216.78	0.00	0.000	0.1219	0.000	0.000	27.4	59.40
115897.88	113945.88	4.204	0.1161	36.209	181.047	0.3	347.69
103739.34	101787.34	3.752	0.1134	33.086	165.429	0.3	311.22
42812.29	40860.29					0.6	
29550.45	27598.45					0.7	
17934.72	15982.72					0.9	
8327.11	6375.11					1.6	
6348.87	4396.87					1.7	
1952.44	0.00					4.8	

APPENDIX 4

This appendix contains the Statworks data file for determination of silicon by ICP-MS. The files contain intensities from eight 0.5 second scans at 28.00 amu. The descriptive statistics provide the average intensity and the standard deviation. The calculation of final silicon concentration in some standard reference materials and some agricultural materials is also given.

StatWorks™ Data

Si by ICP-MS

	D I Water	Blank	0 2 ppm Si	Oyster Tissue	0 5 ppm Si	Oyster Tiss 2
1	4046	17843	33448	67938	57824	82207
2	4116	16679	33812	80915	63062	66706
3	3954	21357	29314	103350	63974	75509
4	3436	22675	27354	127490	56322	93664
5	3576	20401	38248	76637	56910	78589
6	3664	22261	35202	76599	54147	81351
7	3522	19873	33314	84679	65192	77043
8	3436	20265	39269	109450	57504	79235

	0 5 ppm Si	Blank	Pine Needles	1 0 ppm Si	Citrus Leav 2	1 5 ppm Si
1	86510	13287	83301	111640	79171	122110
2	88666	14665	74739	93570	91698	122780
3	83841	10785	89952	114570	87474	116610
4	89768	13669	82131	93526	80695	111120
5	83865	16237	65722	88150	74991	130310
6	80271	14531	73937	84067	92470	113830
7	86046	15337	69872	103730	72493	115650
8	74067	17749	74079	82299	81659	72163

	Tomato Lea 2	Blank	WEP 329-1	Corn Stalk 1	Flour 488-1	Gluten 532 2
1	141910	9855	51835	98878	21077	18733
2	132770	11165	49537	93848	17383	16827
3	118490	9735	44289	95120	14551	16859
4	123340	10565	51021	86872	21413	16647
5	129810	9801	54389	92224	19597	17777
6	135080	10081	46465	84555	17887	18839
7	116740	11115	53049	89588	17581	29000
8	121980	11907	45099	86254	15899	32594

	Corn Kernel 1	Blank
1	10935	7958
2	11757	8544
3	10057	9015
4	9693	7250
5	11999	7126
6	9351	7738
7	10651	6612
8	8917	7510

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: D I Water Observations: 8

Minimum: 3436.000	Maximum: 4116.000
Range: 680.000	Median: 3620.000
Mean: 3718.750	Standard Error: 98.400
Variance:	77460.500
Standard Deviation:	278.317
Coefficient of Variation:	7.484
Skewness: 0.485	Kurtosis: -1.806

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Blank	Observations: 8
Minimum: 16679.000	Maximum: 22675.000
Range: 5996.000	Median: 20333.000
Mean: 20169.250	Standard Error: 729.590
Variance:	4258410.786
Standard Deviation:	2063.592
Coefficient of Variation:	10.231
Skewness: -0.619	Kurtosis: -0.395

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: 0.2 ppm Si Observations: 8

Minimum: 27354.000	Maximum: 39269.000
Range: 11915.000	Median: 33630.000
Mean: 33745.125	Standard Error: 1424.728
Variance:	16238790.696
Standard Deviation:	4029.738
Coefficient of Variation:	11.942
Skewness: -0.248	Kurtosis: -0.478

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS
Variable: Oyster Tissue Observations: 8

Minimum:	67938.000	Maximum:	127490.000
Range:	59552.000	Median:	82797.000
Mean:	90882.250	Standard Error:	7210.529
Variance:		415933837.071	
Standard Deviation:		20394.456	
Coefficient of Variation:		22.441	
Skewness:	0.860	Kurtosis:	-0.321

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: 0.5 ppm Si	Observations: 8
Minimum: 54147.000	Maximum: 65192.000
Range: 11045.000	Median: 57664.000
Mean: 59366.875	Standard Error: 1446.776
Variance:	16745284.411
Standard Deviation:	4092.100
Coefficient of Variation:	6.893
Skewness: 0.418	Kurtosis: -1.634

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Oyster Tiss.2 Observations: 8

Minimum:	66706.000	Maximum:	93664.000
Range:	26958.000	Median:	78912.000
Mean:	79288.000	Standard Error:	2664.465
Variance:			56794986.571
Standard Deviation:			7536.245
Coefficient of Variation:			9.505
Skewness:	0.422	Kurtosis:	2.338

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: 0.8 ppm Si	Observations: 8
Minimum: 74067.000	Maximum: 89768.000
Range: 15701.000	Median: 84955.500
Mean: 84129.250	Standard Error: 1782.892
Variance:	25429626.786
Standard Deviation:	5042.780
Coefficient of Variation:	5.994
Skewness: -1.163	Kurtosis: 1.437

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Blank Observations: 8

Minimum: 10785.000	Maximum: 17749.000
Range: 6964.000	Median: 14598.000
Mean: 14532.500	Standard Error: 735.049
Variance:	4322375.714
Standard Deviation:	2079.032
Coefficient of Variation:	14.306
Skewness: -0.349	Kurtosis: 0.901

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Pine Needles Observations: 8

Minimum: 65722.000	Maximum: 89952.000
Range: 24230.000	Median: 74409.000
Mean: 76716.625	Standard Error: 2784.426
Variance:	62024236.268
Standard Deviation:	7875.547
Coefficient of Variation:	10.266
Skewness: 0.415	Kurtosis: -0.412

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: 1.0 ppm Si Observations: 8

Minimum: 82299.000	Maximum: 114570.000
Range: 32271.000	Median: 93548.000
Mean: 96444.000	Standard Error: 4332.997
Variance:	150198896.857
Standard Deviation:	12255.566
Coefficient of Variation:	12.707
Skewness: 0.466	Kurtosis: -1.367

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS
Variable: Citrus Leav.2 Observations: 8

Minimum: 72493.000	Maximum: 92470.000
Range: 19977.000	Median: 81177.000
Mean: 82581.375	Standard Error: 2605.847
Variance:	54323497.411
Standard Deviation:	7370.448
Coefficient of Variation:	8.925
Skewness: 0.157	Kurtosis: -1.314

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: 1.5 ppm Si Observations: 8

Minimum: 72163.000	Maximum: 130310.000
Range: 58147.000	Median: 116130.000
Mean: 113071.625	Standard Error: 6225.199
Variance:	310024861.125
Standard Deviation:	17607.523
Coefficient of Variation:	15.572
Skewness: -2.151	Kurtosis: 5.462

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Tomato Lea.2 Observations: 8

Minimum:	116740.000	Maximum:	141910.000
Range:	25170.000	Median:	126575.000
Mean:	127515.000	Standard Error:	3113.752
Variance:		77563628.571	
Standard Deviation:		8807.022	
Coefficient of Variation:		6.907	
Skewness:	0.375	Kurtosis:	-1.004

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Blank	Observations: 8
Minimum: 9735.000	Maximum: 11907.000
Range: 2172.000	Median: 10323.000
Mean: 10528.000	Standard Error: 282.320
Variance:	637637.714
Standard Deviation:	798.522
Coefficient of Variation:	7.585
Skewness: 0.676	Kurtosis: -0.836

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: WEP 329-1 Observations: 8

Minimum:	44289.000	Maximum:	54389.000
Range:	10100.000	Median:	50279.000
Mean:	49460.500	Standard Error:	1336.218
Variance:			14283831.714
Standard Deviation:			3779.396
Coefficient of Variation:			7.641
Skewness:	-0.229	Kurtosis:	-1.621

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Corn Stalk 1 Observations: 8

Minimum:	84555.000	Maximum:	98878.000
Range:	14323.000	Median:	90906.000
Mean:	90917.375	Standard Error:	1750.962
Variance:			24526945.411
Standard Deviation:			4952.469
Coefficient of Variation:			5.447
Skewness:	0.280	Kurtosis:	-1.032

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Flour 488-1 Observations: 8

Minimum: 14551.000	Maximum: 21413.000
Range: 6862.000	Median: 17734.000
Mean: 18173.500	Standard Error: 848.369
Variance:	5757844.286
Standard Deviation:	2399.551
Coefficient of Variation:	13.204
Skewness: 0.018	Kurtosis: -0.921

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Gluten 532-2 Observations: 8

Minimum:	16647.000	Maximum:	32594.000
Range:	15947.000	Median:	18255.000
Mean:	20909.500	Standard Error:	2204.147
Variance:			38866096.000
Standard Deviation:			6234.268
Coefficient of Variation:			29.815
Skewness:	1.464	Kurtosis:	0.533

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Corn Kernel 1 Observations: 8

Minimum: 8917.000	Maximum: 11999.000
Range: 3082.000	Median: 10354.000
Mean: 10420.000	Standard Error: 393.280
Variance:	1237352.000
Standard Deviation:	1112.363
Coefficient of Variation:	10.675
Skewness: 0.197	Kurtosis: -1.274

StatWorks™ Data Descriptive Statistics

Data File: Si by ICP-MS

Variable: Blank	Observations: 8
Minimum: 6612.000	Maximum: 9015.000
Range: 2403.000	Median: 7624.000
Mean: 7719.125	Standard Error: 275.761
Variance:	608351.839
Standard Deviation:	779.969
Coefficient of Variation:	10.104
Skewness: 0.431	Kurtosis: -0.302

y = - 4864.329 + 86000x (Calibration Curve)						
Sample	**Ave Intensity**	**Blank**	**Intensity - Blk**	**ppm Si from Calib.**	**Sample Weight**	**Si Conc., ppm**
Oyster Tissue	90882	20169	70713	0.879	0.2538	1731.30
Oyster Tissue 2	79288	20169	59119	0.744	0.2506	1484.42
Pine Needles	76717	14532	62185	0.780	0.25	1559.29
Citrus Leaves 2	82581	14532	68049	0.848	0.2514	1686.22
Tomato Leaves 2	127515	14532	112983	1.370	0.0854	8022.94
WEP 329-1	49460	10528	38932	0.509	0.0757	3363.67
Corn Stalk 1	90917	10528	80389	0.991	0.2652	1869.00
Flour 488-1	18174	10528	7646	0.145	0.5002	145.41
Gluten 532-1	20909	10528	10381	0.177	0.5016	176.71
Corn Kernel 1	10420	7719	2701	0.088	0.5013	87.74